1973

A nuclear magnetic resonance and vibrational spectroscopic investigation of adducts of selected phoshine donors with boron hilide acids.

Bernard. Rapp
University of Windsor

Recommended Citation

Rapp, Bernard., "A nuclear magnetic resonance and vibrational spectroscopic investigation of adducts of selected phoshine donors with boron hilide acids." (1973). *Electronic Theses and Dissertations*. 688.
https://scholar.uwindsor.ca/etd/688

A NUCLEAR MAGNETIC RESONANCE
AND
VIBRATIONAL SPECTROSCOPIC INVESTIGATION
OF ADDUCTS OF SELECTED PHOSPHINE DONORS
WITH BORON HALIDE ACIDS

By

Brother Bernard Rapp, M.Sc.

A Dissertation
Submitted to the Faculty of Graduate Studies through the
Department of Chemistry in partial fulfillment of the
requirements for the Degree of Doctor of Philosophy
at the University of Windsor

Windsor, Ontario.
1973

To my confreres,

the Christian Brothers

FOREWORD

The following account is the result of a research investigation undertaken in the chemical laboratories of the University of Windsor from August, 1970 to July, 1973. Each of the following chapters concentrates on a specific aspect of that investigation. Since the chapters stand relatively independent of one another, it seemed appropriate to reference each individually. Hence, references are to be found at the conclusion of each chapter rather than in a general bibliography located at the end of the entire work.

In order to draw attention to the essential aspects of the investigation it was decided to place the more general features of the Experimental Procedures in the APPENDIX along with several tables of raw data bearing on various segments of the work. Only the essential and most immediate experimental phases of the investigation are included in each specific chapter.

Since the investigation touched on several aspects of the phosphorus-boron dative bond it was thought desirable to include a general background study pertaining to this subject. This literature survey can be found in Chapter I in which an effort was made to give as thorough a review of the theoretical and research developments on the P-B bond as possible within appropriate space limitations.

The author wishes to express his gratitude and appreciation for the assistance that he has received in the course of this investigation from several persons and groups in the Chemistry Department of the

University of Windsor. The graduate students in the inorganic laboratory where the research was conducted contributed much by their continued interest and helpful suggestions throughout the course of the work. The various members of the Graduate Faculty were of significant assistance by their willingness to listen, to offer help based on experience, and give advice. The author wishes to explicitly acknowledge the help of Dr. J. L. Hencher of this Department who spent many hours in checking the assignments of the vibrational spectra by means of normal coordinate analysis.

Special appreciation is due to Dr. John E. Drake under whose supervision this work was carried out. His interest and many helpful discussions contributed substantially to the progress of this work.

Windsor, Ontario
July, 1973

TABLE OF CONTENTS

CHAPTER

I. THE PHOSPHORUS-BORON DATIVE BOND--A BACKGROUND 1

VI. THE VIBRATIONAL SPECTROSCOPIC INVESTIGATION OF THE PHOSPHINE BORON TRIHALIDES 132

APPENDIX

LIST OF TABLES

Table Page

Table Page

LIST OF FIGURES

Figure

ABSTRACT

A series of 24 derivatives of phosphine borane of general formula $R_nPH_{3-n}BX_3$ (R = Me, Ph; n = 0, 1, 2; X = H, F, Cl, Br, I) have been prepared. Approximately 30 adducts of general representation $Me_nPH_{3-n}BX_2Y$ and $Me_nPH_{3-n}BXY_2$ (X ≠ Y = H, F, Cl, Br, I; n = 0, 1) comprising "mixed species" have also been prepared. Both very low solubility and generally weak P-B bonds are typical characteristics of all adducts.

Nuclear magnetic resonance spectroscopy of various nuclei: ^1H, ^{11}B, ^{31}P, and ^{19}F, is utilized to study the several adduct series. Infrared and Raman spectroscopy are employed in the vibrational analysis of the adduct series PH_3BX_3 (H = ^1H, ^2H; X = Cl, Br, I).

Trends in the ^1H n.m.r. parameters of the five $R_nPH_{3-n}BX_3$ series (R = Me, Ph; n = 0, 1) are presented. Chemical shifts and coupling constant data are examined as to their utility as indicators of relative acidity and basicity of acceptor and donor moieties. Temperature dependent spectra are examined as qualitative indicators of adduct stability.

Halogen redistribution to form mixed adduct species is also studied by ^1H n.m.r. Some 15 boron halide acids, BX_2Y and BXY_2 are placed in an order of decreasing Lewis acidity as determined on the basis of $\delta_{^1H}$ and J_{PH} for two adduct series (PH_3 and $MePH_2$). Halogen-hydrogen exchange on boron is similarly studied. Finally, equilibrium constants for halogen redistribution reactions are evaluated by means of ^1H n.m.r. Assuming that the mole percent of each component in the mixture is proportional to the area under each respective peak, equilibrium constants are obtained. Comparison is made with those obtained from redistribution studies of "free" boron trihalides. Results are also compared to the "random distribution" case.

^{11}B n.m.r. parameters are obtained for both the 24- and the 30-component adduct systems. Again, chemical shift and coupling constant (J_{PB}) values are investigated in terms of their usefulness as predictive indicators of Lewis acidity and basicity, as well as of adduct stability. The results are compared with those derived from the ^1H n.m.r. investigation.

^{31}P n.m.r. parameters are presented for only those systems which are sufficiently soluble to permit investigation, namely, $R_nPH_{3-n}BH_3$ (R = Me, Ph; n = 0, 1, 2) and PH_3BH_2X and PH_3BHX_2 (X = Cl, Br, I). Chemical shift and coupling constant data are examined on the basis of their "internal consistency" with the nuclear magnetic resonance data obtained in the ^1H and ^{11}B studies.

^{19}F n.m.r. parameters are obtained on all BF_3 adducts. Chemical shift values of fluorine are related to adduct stability and donor basicity. J_{BF} and J_{PBF} values are discussed.

A vibrational analysis of the adduct series PH_3BX_3 and PD_3BX_3 is undertaken in an effort to assign the fundamental vibrational modes. The Raman investigation is carried out on solid and solution (CH_3I and CH_2Cl_2) samples. Polarization data is obtained where possible. The infrared study is carried out on Nujol mulls and CsI pellets of the solid and on CH_3I and CH_2Cl_2 solutions of the adducts. Assignments are checked for agreement with calculated Product Rule ratios.

CHAPTER I

THE BORON-PHOSPHORUS DATIVE BOND--A BACKGROUND

The nature and characteristics of the coordinate bond as found in molecular addition compounds have been the focus of considerable discussion and rather intensive investigation for a relatively long period of time. The Group III elements of the Periodic Table, because of their electronic structure, form a wide variety of compounds which have found extensive use as acceptor species in dative bond studies. This is especially true of boron as attested to by the rather large number of reviews concerned with the coordinate link formed by compounds of trivalent boron. Some of these have dealt with the addition compounds of a specific acceptor species such as boron trifluoride, BF_3,[1,2] boron trichloride, BCl_3,[3] boron tribromide, BBr_3, and boron triiodide, BI_3,[4] and borane,* $[BH_3]$.[5,6] Others have taken a more general approach by utilizing the data associated with one class of acceptor molecules, for example, the alkylboranes,[7,8] to trace the variations in dative bond properties with systematic changes in the substituents on boron.

In most surveys one notes a considerable variety in the selection of donor species in dative bond investigations. Among compounds of the First Row elements those of nitrogen and oxygen have found extensive use. The nitrogen-boron adduct, H_3NBF_3, was in fact among the earliest known compounds of this type, having been studied by Davy.[9] Donor molecules

---

*The $[BH_3]$ species, variously called borane or borine, does not exist as the stable four-atom entity except in combination with other chemical moieties. Hence brackets are employed to indicate the hypothetical formulation of the monomer. Diborane, B_2H_6, is the stable hydride of boron.

of Second Row congeners were not employed in addition-type reactions with boron acceptors until considerably later. The phosphine adduct of boron trichloride was first prepared by Besson[10] in 1890 by reacting equal volumes of PH_3 and BCl_3 at temperatures lower than 20°C.

1. The Structure of "Diborane Diphosphine." It was not, however, until 1940, well after Lewis had formulated his electronic interpretation of acid-base behavior,[11,12] that Gamble and Gilmont set the stage for a more intensive study of the dative bond in molecular addition compounds. They reacted phosphine with diborane at low temperatures to produce the white crystalline material which was called "diborane diphosphine" on the basis of reaction stoichiometry.[13] With some reservations the authors tentatively proposed a phosphonium type formulation for the new compound because of its chemical similarity to PH_4Br in its reactions with liquid ammonia. Thus the chemical formulation for the new compound was given as $PH_4^+(BH_3PH_2BH_3)^-$. The model used as a basis for this proposal was the then-accepted structural postulate for the analogous diborane diammine, $NH_4^+(BH_3NH_2BH_3)^-$.[14] The possibility of the monomeric solid, PH_3BH_3, was not ruled out; however, its existence in the gas phase could not be established. Numerous studies subsequently conducted on the compound, $B_2H_6 \cdot 2PH_3$, indicated that neither the above formulation nor the alternate $(PH_3BH_2PH_3)^+BH_4^-$ based on the revised structure of the "diammoniate of diborane"* could adequately explain new data. A gas phase kinetic

---

*The structure $(NH_3BH_2NH_3)^+BH_4^-$ was proposed after the discovery of the borohydride ion by Schlesinger and coworkers[15] but was discarded as inadequate.[16] Later work, however, gave additional support to the borohydride model.[17]

investigation of the reaction between phosphine and diborane was conducted in an effort to determine the heat of dissociation of diborane.[18] The proposed mechanism assumed the formation of a P-B addition compound:

$$B_2H_6 + PH_3 \rightleftarrows PH_3BH_3 + BH_3$$
$$BH_3 + PH_3 \rightleftarrows PH_3BH_3 .$$

It was not, however, until 1961 that a crystallographic investigation of the compound by McGandy gave unequivocal evidence for the monomeric formulation for the solid compound.[19] The P-B bond length for the adduct PH_3BH_3 was found to be 1.93 Å. But neither the HLH bond angles nor the L-H bond distances (L = P, B) were clearly determined. The tendency of the solid adduct to dissociate into its constituent molecules at ambient temperature and pressure, or to liquify at pressures somewhat in excess of atmospheric contributed to the difficulties associated with this direct method of structural analysis. Subsequent studies of a more indirect nature were required and were, in part, aided by the tendency of PH_3BH_3 to liquify under pressure. Thus ^1H and ^{11}B n.m.r. studies on the neat liquid[20] gave spectral evidence consistent with the monomeric interpretation. Both infrared and Raman spectroscopic data indicated that the same structure is maintained in the solid phase.[20] A later Raman investigation of the neat liquid lent additional support for a simple C_{3v} structural conformation for the acid-base monomer.[21] A ^1H n.m.r. study of PH_3BH_3 in solution established that the compound maintains its monomeric structure in the presence of CH_2Cl_2 solvent.[22]

It was not until early 1973 however that the structural details of PH_3BH_3 were precisely determined by means of the microwave spectrum of the gaseous monomer at at -70°C. By means of this indirect method, Durig and coworkers[23] completed the structural determination initiated twelve years earlier with the X-ray crystallographic investigation.[19] The structural parameters of phosphine borane are recorded in Table I - 1. It is to be noted that the P-B bond distance in the solid phase is essentially the same as in the gaseous phase. Hence the dative bond in phosphine borane is apparently little affected by change of physical state.

TABLE I - 1

The structural parameters of phosphine borane as determined from the microwave spectrum; bond distances in Å ± 0.003 Å; bond angles in degrees ± 0.2°

Bond Distances		Bond Angles	
P - B	1.937 ± 0.005	PBH	103.6
B - H	1.212	BPH	116.9
P - H	1.399	HBH	114.6
		HPH	101.3

The structural determination of phosphine borane, at least as to its basic geometry, is in a sense fundamental to the further investigation of the P-B bond in its various derivatives. Unless structural similarity maintains between the compounds studied, it would hardly be of profit to undertake the rationalization of either anomalous or consistent behavior in a given series. With structural similarity of the adducts as a basic assumption, a systematic investigation of the various properties such as relative stabilities, heats of formation, exchange processes, dipole moments, charge transfer, vibrational and magnetic resonance spectra can all shed light on the nature of the P-B interaction.

2. Phosphino- and Aminoboranes. Although this study is concerned with a specific group of addition compounds, namely, phosphine borane and its derivatives, it is appropriate at this point to mention that treatment of a specific Group V donor molecule with a boron Lewis acid does not always result in the formation of a 1:1 adduct. As might be expected a significant displacement of charge accompanies adduct formation and this could have the effect of introducing a substantial degree of ionic character in the substituents on both donor and acceptor atoms. Thus if conditions warrant, a 1:1 adduct may indeed react in an intermolecular fashion to yield cyclic or polymeric products. Borazine (or borazole), $B_3N_3H_6$, was originally prepared by Stock and Pohland[24] and was assumed to possess a polymeric cyclic structure analogous to benzene with an alternating B-N ring structure. The correctness of this assumption was later confirmed by electron diffraction studies.[25] The synthesis of this compound was explained by assuming an initial formation of the ionic adduct $^{\delta+}H_3NBH_3^{\delta-}$ followed by a stepwise elimination of hydrogen:[26]

$$H_3NBH_3 \xrightarrow{-H_2} H_2NBH_2 \xrightarrow{-H_2} HNBH = \tfrac{1}{3}\,B_3N_3H_6 .$$

Wiberg and co-workers [27,28] found that thermal decomposition of the compounds $Me_nNH_{3-n}BMe_3$ ($Me \equiv CH_3$; $n = 1, 0$) led to cyclic six-membered rings with the elimination of methane,

An analogous chemistry has been observed with respect to some phosphorus-boron addition compounds. Burg and Wagner[29] found that the adduct Me_2PHBH_3 loses hydrogen upon heating to form cyclic trimers and tetramers of general formula $(Me_2PBH_2)_x$. When intermolecular processes occur between addition compounds formed by boron halides with hydrogen-containing phosphine ligands, HX is eliminated.[30] The cyclic structures of these P-B systems have been confirmed by electron diffraction studies.[31,32] The P-B bond in compounds of this type differs considerably in its properties from that found in addition compounds. Unlike the latter, phosphinoboranes are typified by resistance to dissociation and thermal decomposition, insensitivity to air and low reactivity towards acids and bases in hydrolytic bond cleavage reactions. The unusually inert character of these compounds is attributed to a supplemental (p-d)π bonding between boron and phosphorus with some charge contribution from the B-H bonds.[29] A thermochemical investigation has revealed that similar differences exist between the coordinate bond in nitrogen-boron adducts and its counterpart in covalent N-B compounds of the type $B(NR_2)_3$[33] and cyclic polymeric species.[34] The mean N-B bond dissociation energy in these latter type compounds is found to range between 80 and 90 kcal/mole. On the other hand, in typical addition compounds like Me_2HNBMe_3 the bond dissociation energies lie between 13 and 28 kcal/mole ($\bar{D}$ = 19.3 kcal/mole for Me_2HNBMe_3).[33] Supplemental (p-p)π back-donation may also play a part in the higher stability of the covalent linkages but it should be noted that this argument has also been employed to rationalize the differences in relative stabilities between adducts themselves.[35] Internuclear bond distance studies on nitrogen-boron compounds of both types have shown that while the N-B bond distance for donor-acceptor compounds is in the range of 1.6 Å,[36] that for borazine is 1.44 Å[37] and for B-trichloroborazine it is 1.41 Å.[34] This is in contrast to the nearly identical P-B bond lengths in the "dative" bonded adducts, PH_3BH_3 and $MePH_2BH_3$ and the "covalent" bonded cyclic trimer $(Me_2PBH_2)_3$. In the 1:1 addition compounds the P-B bond length is 1.937 Å[23] and 1.906 Å,[38] respectively; in the polymer it is 1.92 Å.[32]

The contrasts and similarities in the structural data given above highlight a point of difficulty which intermittently appears in the discussion of molecular adduct systems. The difference in bond length parameters between N-B adducts and N-B polymers may be interpreted as reflecting a real difference between the dative bond (formed by the donation of both electrons by one of the bonding atoms) and the typical covalent bond (formed by the mutual donation of one electron from each bonding atom). The similarity in bond lenghts of the P-B systems cited above may be taken as evidence that no essential differences exist between bond types once interaction has occurred.

Evidence based on charge transfer experiments has been interpreted as indicating a distinction between the two types of bonds. The degree of ionicity in dative bonds as a result of charge transfer is found to be greater than in the analogous covalent linkages.[39] Adduct formation between compounds of Group III elements (B, Al, Ga) and compounds of Groups V and VI elements (N, P, O, S) has been found to result in bond ionicities ranging from a maximum of 0.94 ± 0.05 e (P→B) to a minimum of 0.52 ± 0.01 e (O→Ga). Although a high ionicity is found in phosphorus-boron adducts as a result of charge transfer (R_3PBH_3 and R_3PBCl_3 have values of 0.92 e and 0.95 e, respectively; R ≡ unspecified alkyl); in covalent systems of the type $B(PR_2)_3$ or in cyclic systems little influence on bond polarity is observed beyond the effects which can be expected on the basis of electronegativity differences (0.01 e in polymeric P-B compounds). Similarly, nitrogen-boron adducts exhibit a bond polarity of 0.81 ± 0.10 e as opposed to 0.13 e in cyclic systems. It might be observed, however, that the differences in bond ionicity between analogous systems may not be due so much to real differences in bond type as to the cyclic or otherwise symmetric structure of the "covalent" systems where delocalization of charge concentrations might readily occur.

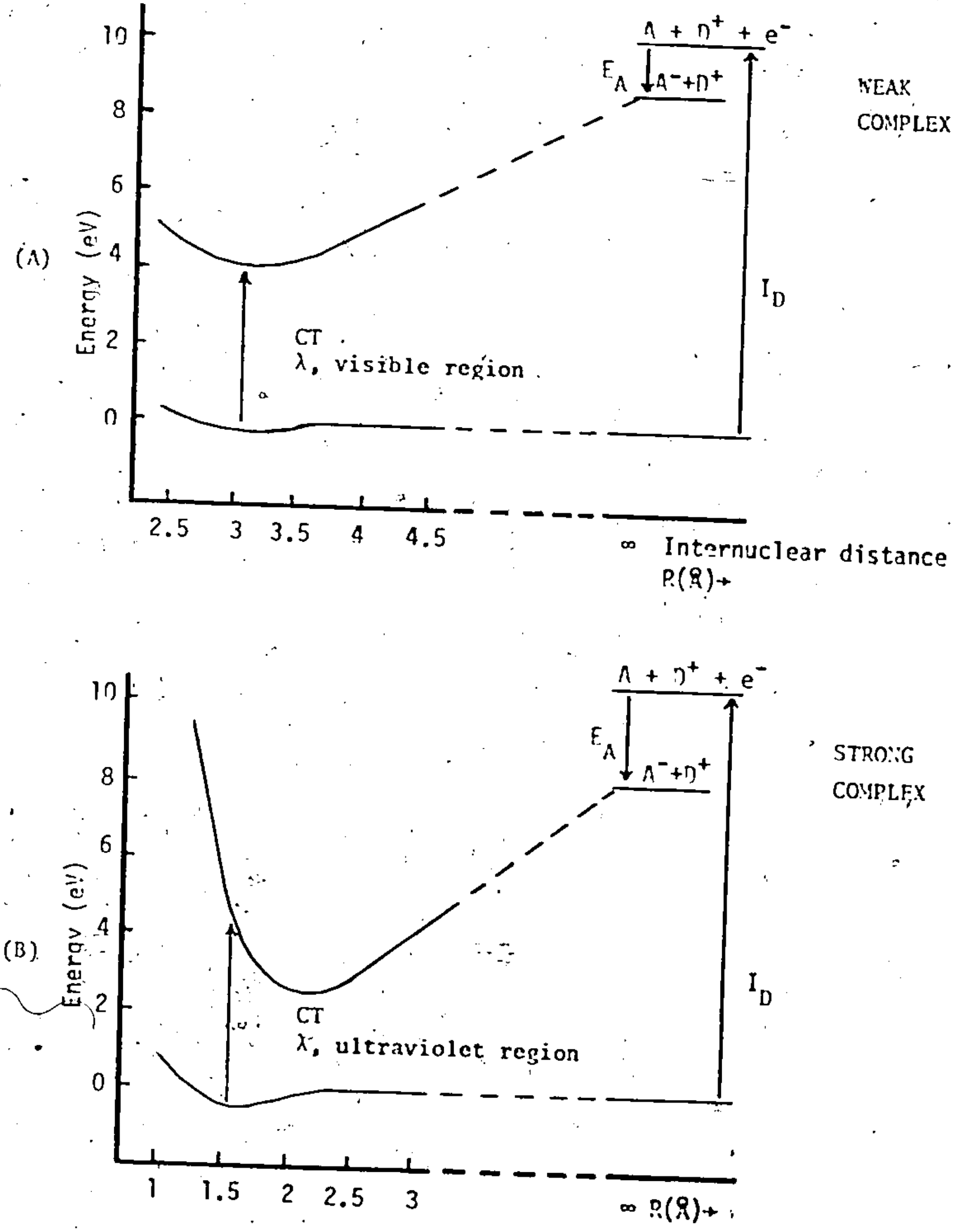
3. Theories of Donor-Acceptor Bonding. The properties of the donor-acceptor bond as found in simple 1:1 adduct systems were placed on a theoretical basis by R. S. Mullikan.[40] Using the valence bond model, he described the coordinate bond as a resonance condition between (1) a non-bonding repulsive state of the respective molecules, and (2) a quasi-covalent bonding condition resulting from the interaction of the ions $D\cdot^+$ and $\cdot A^-$. The total wave function for the complex, the resonance condition, was taken as the sum of the two opposing states:

$$\Psi_{res(D^+A^-)} = a\,\Psi_{0(D,A)} + b\,\Psi_{1(D^+A^-)} .$$

Ψ_0 represents the "no-bond" wave function where both molecules are in totally symmetric ground states; that is, all valence electrons are paired. For $A = BX_3$, this corresponds to its trigonal sp^2 configuration; for $D = PH_3$, the totally symmetric electronic ground state would coincide with the p^3 orbital description. The relative contributions of "a" and "b" terms are dependent upon the distance of separation between the interacting pair. At large distances the non-bonding contribution predominates. At some intermediate D-A distance, a balance is struck between the contributions and complex formation ensues. Additional energy adsorption by the complex results in raising $\psi_{res(D^+A^-)}$ to an excited state where the contribution from "a" is << "b".[41] The energy of either a strong or a weak donor-acceptor complex in the excited state is a summation of the energy required to remove an electron from the donor species ($I_D \equiv$ ionization energy, donor), the energy released following acceptance of the electron by the acceptor molecule ($E_A \equiv$ electron affinity, acceptor), and finally the coulombic energy released in bringing the two ions, A^- and D^+, to their equilibrium distance of separation. In this state b/a is large, (Figure I - 1). In the ground state, however, the ratio of "b" to "a" is only slightly greater than unity. Hence, the actual extent of charge transfer in the ground state is thought to be relatively small, although greater in the stronger complex. An essential difference between the two adduct types lies in the depth of the ground state potential energy well, implying that the "b" contribution to the total wave function of the strong complex is somewhat greater than that in the weak adduct. In the strong complex, the non-alignment of potential energy wells reflects the difference in equilibrium geometry of the donor and acceptor species in the two energy states. In the excited state, both moieties are in a near-tetrahedral configuration, whereas in the ground state, a geometrical arrangement exists which is a compromise between ψ_0 and ψ_1.[42]

Skinner and Smith made use of this model in discussing the results of their previously cited thermochemical study[33] and Kistiakowsky and

Figure I-1 -- Potential energy curves for (A) the weak benzene-iodine charge transfer complex, and (B) the strong Me_3NBF_3 charge transfer complex.



Williams[43] in their gas phase study of BF_3-Me_nNH_{3-n} reaction kinetics were able to apply the model in interpreting their data. Reaction rate was observed to increase in nearly regular fashion with increasing methyl substitution: $NH_3 < MeNH_2 < Me_3N < Me_2NH$. The energies of activation decreased proportionately from 4 to 2 kcal/mole. The 4 kcal upper limit was interpreted as the maximum potential energy present at the intermediate D-A distance. Subsequent lowering of the potential energy barrier was attributed to enhanced polarizability of the unshared electron pair on the donor as a result of inductive effects. A redistribution of the "a" and "b" contributions led to lower activation energies and stronger complexes.

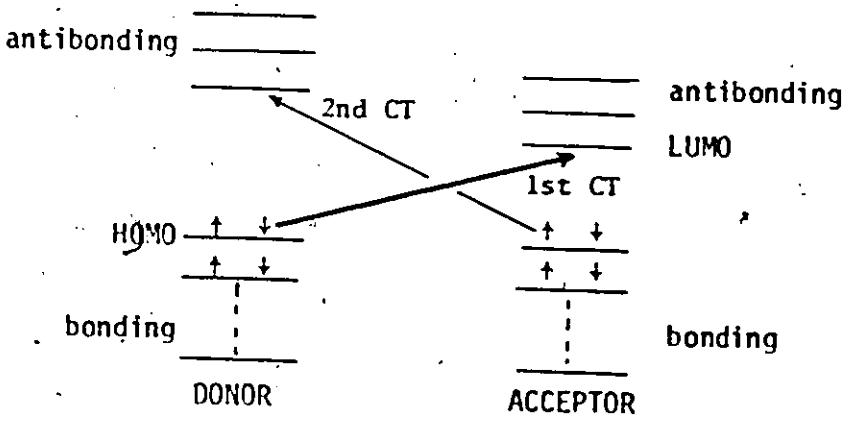
By means of the valence bond model, Mulliken was able to assemble and explain the observed experimental facts in a satisfactory manner. Although the theory specifically covered both weak and strong adduct systems, it has been pointed out that a molecular orbital description is better suited to the interpretation of the strong complex system.[44] In the case of the former, it is only in the excited state that bond ionicity is a dominant factor in bonding:

$$D + A \rightarrow [\psi(D,A);\ \underset{\text{minimal influence in ground state}}{\psi(D\cdot^{+}\cdot A^{-})}] \xrightarrow{h\nu} [\psi(D,A):\ \underset{\text{major contribution to excited state}}{\psi(D\cdot^{+}\cdot A^{-})}]$$

In complexes of this type a substantial portion of the ground state binding energy (2 - 10 kcal/mole) may reside in London (dipole-induced dipole) dispersion forces.[45,41] In the stronger adducts, such as are the focus of this study, $\psi(D\cdot^{+}\cdot A^{-})$ contributes somewhat more significantly to the ground state binding energy (12 - 30 kcal/mole).[8] For these a valence bond formulation similar to that given for heteronuclear diatomic molecules,[46] $\psi = \psi_{cov} + \lambda\psi_{ion}$, would not be inappropriate (where $\lambda \equiv$ a constant determining the asymmetry of charge distribution or polar characteristics of the bond).

The molecular orbital approach for weak complexes as proposed by Dewer and Lepley[47] postulates that little change takes place in orbital energies of the donor and acceptor when adduct formation occurs. Charge transfer is interpreted as occurring between the highest occupied molecular orbital (HOMO) of the donor and lowest unoccupied molecular orbital (LUMO) of the acceptor. This conceptualization permits a more facile explanation of secondary spectral bands appearing in the electronic spectra of the adducts (Figure I - 2).

Figure I - 2 -- Orbital energies and transitions in a molecular complex formed by donor and acceptor species.[47]



The term "π-complex" has been applied to the weak molecular addition compounds because a portion of their stability is thought to be due to back-coordination involving interactions between filled orbitals of the acceptor and empty orbitals of the donor.[47] The use of the term implies a basic distinction between compounds of this type and the stronger adducts. Whether such a distinction has a basis in actual fact is a point of controversy. Thus, Briegleb[48] in his work on donor-acceptor complexes assumes an essential difference between adducts formed by bases and weak acids like iodine and by bases and strong acids like the boron trihalides. This position is experimentally supported in a very recent report on BF_3 adducts of aromatic aldehydes.[49] Yet, in a recent review on acid-base adducts,[50] the author explicitly discusses the "illusion" that persists in assuming an essential difference between what are called weak "π-complexes" and strong "σ-σ-complexes."

4. Methods of Assessing Adduct Stability and Acid or Base Strength. The various methods of assessing the stability of addition complexes or of evaluating relative acidity and basicity have been amply reviewed.[8] Only those methods will be briefly discussed here which have some relevance to the material in subsequent chapters.

The gas phase dissociation of an adduct into its component parts was early recognized as a natural measure of the stability of the donor-acceptor bond. Furthermore, for a given acid-base series, where one component is held constant while the other is varied in regular fashion, this parameter should provide a reasonably good assessment of Lewis acidity or basicity.* Brown et al.[52] made precise measurements of the

---

*In a discussion of his acid-base theory[51] Lewis pointed out that neither acid or base strength could be viewed in absolute terms, but must always be considered in terms of the conjugate with which interaction occurs.

thermal dissociation parameters of the adduct series $Me_nNH_{3-n}BMe_3$. The observed degree of dissociation, α, as a function of temperature permitted the calculation of K_p, ΔH, ΔG^o, and ΔS. The values which they obtained together with those of the analogous Me_nPH_{3-n} system taken from another source[53] are given in Table I - 2.

TABLE I - 2

Gas phase dissociation data for the BMe_3 adducts of Me_nLH_{3-n} (L = N, P; n = 0, 1, 2, 3)[3]

COMPOUND	ΔH	ΔS	ΔG^o	K_p
H_3NBMe_3	13.75 $\frac{kcal}{mole}$	39.9 $\frac{cal}{mole\text{-}deg}$	-1.13 $\frac{kcal}{mole}$	4.62
MeH_2NBMe_3	17.64	40.6	+2.46	0.0360
Me_2HNBMe_3	19.26	43.6	+2.89	0.0214
Me_3NBMe_3	17.62	45.7	+0.56	0.472
H_3PBMe_3	(not formed at temperatures as low as -78°C)			
MeH_2PBMe_3				∞ at 20°C
Me_2HPBMe_3	11.41	35.1	-1.69	9.8
Me_3PBMe_3	16.47	40.0	+1.52	0.128

The enthalpy change, ΔH, itself can be a reliable measure of adduct stability only if the respective entropies of dissociation are relatively close.

The anomalous order of observed stability, $H_3NBMe_3 < MeH_2NBMe_3 < Me_3NBMe_3 < Me_2HNBMe_3$, was explained by Brown in terms of the B-strain theory.[52a,54] According to this model, Me_3N, although potentially the strongest base of the entire series in view of the inductive effects of the methyl group, is not able to bind as strongly as would be expected because of steric crowding among the six methyl groups of the adduct. When the donor series Me_nPH_{3-n} was tested against the same reference acid the order of stability (and hence, basicity) was observed to increase in regular fashion with increasing methyl substitution.[53,55] The results were interpreted as supporting the validity of the B-strain theory since less steric hindrance occurs among the methyl groups attached to the larger phosphorus atom and those attached to boron. Quite recent gas phase studies of amine basicities in donor-acceptor reactions[56,58] are in good agreement with the regular ordering of basicity as proposed by Brown rather than that actually observed in the solution phase. However, gas phase studies have also shown that orders of acidity and basicity can not be explained solely in terms of any one inductive effect.[59,60] This is of particular relevance in interpreting the effects of alkyl substitution on phosphorus in phosphine borane adducts.

Displacement reactions have been employed to qualitatively evaluate relative stabilities of adducts and strengths of acids and bases.[61-64] Most of these studies have employed ^1H and ^{11}B nuclear magnetic resonance methods to follow the course of such reactions and to identify reacting species. Proton n.m.r. is generally preferred when the systems are of limited solubility because of the enhanced sensitivity of the ^1H nucleus to the imposed magnetic field as contrasted with that of the ^{11}B nucleus.[65] On the other hand, ^1H n.m.r. spectra of mixed systems can be quite complicated by overlapping resonance signals and the same reaction may be more easily followed by observing the ^{11}B n.m.r. spectrum.[a]

Since adduct formation generally results in significant rehybridization of the donor and acceptor bonding orbitals, it is to be expected that the strength of the interaction will be reflected in the extent of rehybridization. Nuclear magnetic resonance coupling constant values are directly affected by the hybridization state of bonded nuclei. Thus, as shall be seen in the body of this work, the magnitude of the phosphorus-hydrogen coupling constant can serve as an index of Lewis acidity or of dative bond strength. Less use is made of boron-hydrogen coupling constants because of their reduced intensity. The resonance peaks of protons attached to boron lack the sharpness which is normally observed in ^{1}H n.m.r. spectra. Signal broadening is attributed to the effects of the nuclear quadrupole moment of the boron nucleus. This moment interacts with the fluctuating electric field gradients produced at the boron nucleus by the tumbling of the molecules. As a result, the ^{11}B nucleus changes its energy states rapidly, thereby giving rise to a broadened resonance signal.[66]

The low solubility of many 1:1 boron-phosphorus adducts has imposed limitations on the use of nuclear magnetic resonance as an analytical tool in this area of study. The BF_3 and $[BH_3]$ adducts are generally the most soluble members of various BX_3 series and for this reason most of the literature to date pertains to the n.m.r. parameters of adducts of these two acceptors.

In addition to the extensive use of ^{1}H and ^{11}B n.m.r. methods, ^{31}P and ^{19}F magnetic resonance studies have also found considerable use in efforts to evaluate adduct stabilities and acid-base strengths. This material as well as that concerned with infrared and Raman studies can not be adequately surveyed here. It will be systematically reviewed in the appropriate chapters of this investigation.

5. The Relative Strengths of Acceptor Species. The relative strengths of Lewis acceptor species, as evaluated by the methods enumerated above, are observed to follow in general accord with the electronegativities of the groups attached to boron. Thus, if electronegative groups are located on boron, complex formation is facilitated. On the other hand, when electron-donating groups are placed on boron, the complexes formed are often quite weak.[8] However, in the case of those Lewis acids which are central to this work, namely, the boron trihalides, acidities do not increase with increasing electronegativity. The relative order of acceptor ability, once thought to be $BF_3 > BCl_3 > BBr_3 > BI_3$,[4] has in actual fact been found to be opposite to that expected on the basis of electronegativity considerations.[67,68] The rationalization of an order of acidity $BI_3 > BBr_3 > BCl_3 > BF_3$ is made in terms of the delocalized $(p\text{-}p)\pi$ bonding between the vacant p_z orbital on boron and the occupied non-bonding orbitals on the adjacent halogens.[69] In order for any BX_3 species to act as an effective acid it must lose its planar sp^2 configuration and assume a near-tetrahedral arrangement of atoms around boron. For this to happen energy is required to overcome the bond energy resulting from the delocalized π-system. Additional energy is needed to effect small changes in the BX σ-bonding when the boron orbitals rehybridize

from sp^2 to sp^3 configuration. The sum total of these two terms is called the reorganization energy. All but a very small part of this is accounted for by the π-system. Except for BI_3 the reorganization energies of all the boron trihalides have been determined (Table I - 3). Assuming that the π-bond energy is directly proportional to the out-of-plane B-X bending force constants,[70] the reorganization energy of BI_3 can be closely estimated (Figure I - 3).

TABLE I - 3

The π-bonding and reorganization energies (kcal/mole) and the out-of-plane bending force constants (10^5 dynes/cm^2) for the boron trihalides.

	BF_3	BCl_3	BBr_3	BI_3
π-Bonding Energy	47.8	29.9	25.7	
Reorganization Energy	48.3	30.3	26.2	
Out-of-plane Bending Force Constant	0.86	0.41	0.29	0.24

A reorganization energy of about 24 kcal/mole for BI_3 would seem to be a reasonable estimate on the basis of the extrapolated π-bond energy value (Figure I - 3).

Two recent papers, one based on ionization potential determinations by electron impact and MO calculations[71] and the other based on nuclear quadrupole resonance data,[72] have suggested that the order of back-donation from halogen to boron is opposite to that implied above, and is in fact $BI_3 > BBr_3 \simeq BCl_3 > BF_3$. Bassett and Lloyd[73] have however

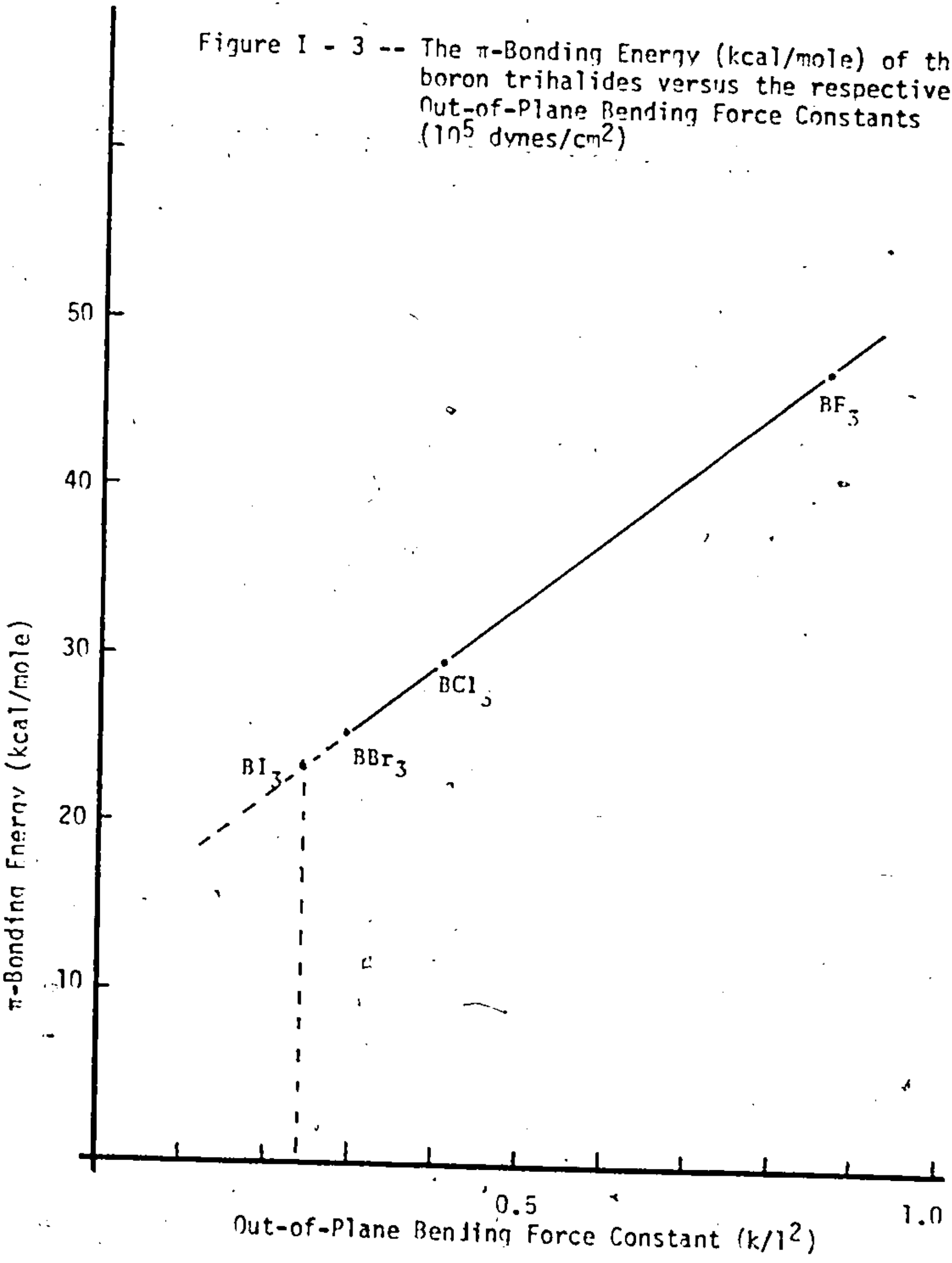


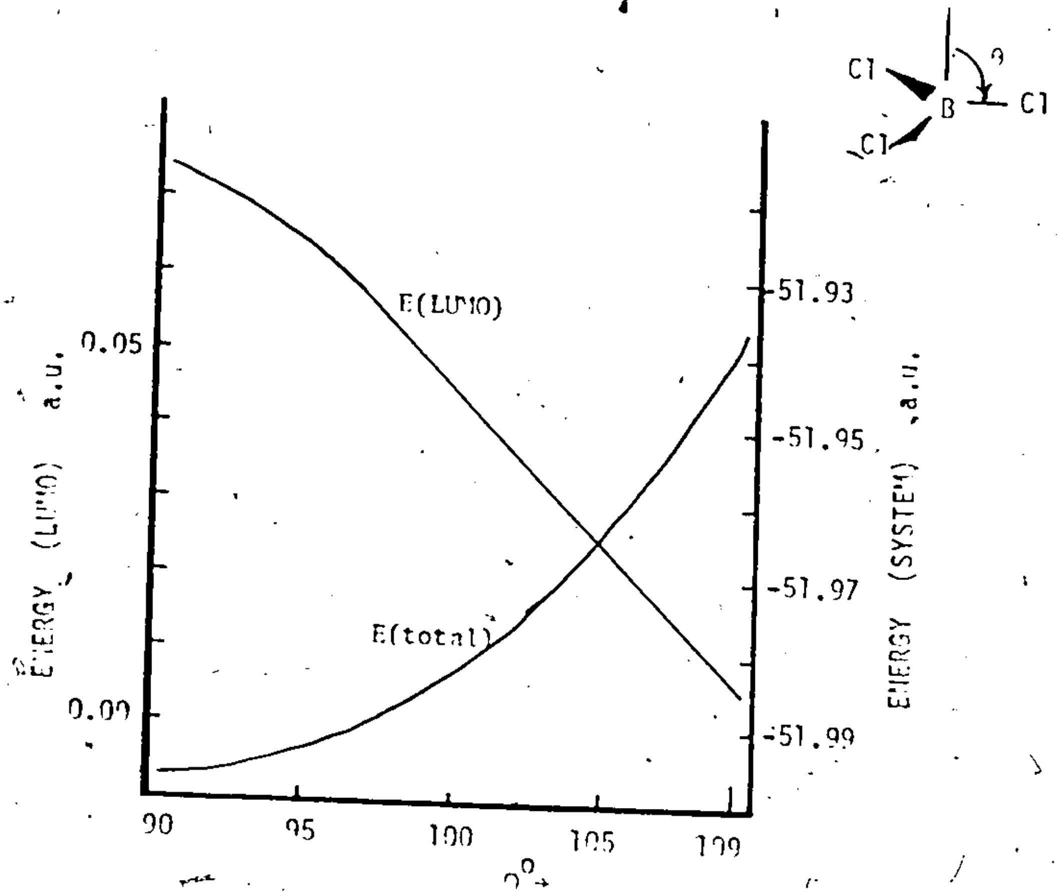
Figure I - 3 -- The π-Bonding Energy (kcal/mole) of the boron trihalides versus the respective Out-of-Plane Bending Force Constants (10^5 dynes/cm^2)

pointed out that the stabilization due to this back-bonding is in the opposite order and therefore consistent with BI_3 requiring the least deformation energy.

It is clear that the decreasing trend in reorganization energy parallels that of increasing acidity in the boron trihalides. It is in these terms that the acceptor power of the boron trihalides toward various Lewis bases is explained. The established order of Lewis acidity of these species received additional confirmation in a recent electron spin resonance study of the BX_3 complexes of the nitroxide free radical.[74] The order of acidity is $BBr_3 > BCl_3 > BF_3 = AlCl_3$.

In a vibrational spectroscopic investigation of the acetonitrile complexes of boron trihalides[75] the relative order of BX_3 acidity is attributed to more than differences between reorganization energies. The model proposed is of particular interest because of its possible relation to the molecular orbital bonding theory of addition compounds developed by Dewer and Lepley.[47] In any BX_3 acceptor the energy of the lowest unoccupied molecular orbital (LUMO) is calculated to decrease with increasing distortion from planarity (Figure I - 4). The total energy of the system however increases by reason of the energy required to distort or reorganize the molecule. The increase in total energy of the system is amply compensated for by the formation of the donor-acceptor bond. The added dimension to the discussion of relative acidities lies in the fact that the respective energy curves of the various BX_3 species are not appreciably different but the energies of the lowest unoccupied molecular orbitals are. Thus the LUMO energy of BF_3 is 2.3 to 3.3 eV higher than that of BCl_3. Consequently, BCl_3 should function as a better electron

Figure I - 4 -- Variations in the energies of the lowest unoccupied molecular orbital and of the entire system with degree of distortion from planarity for the BCl_3 system.

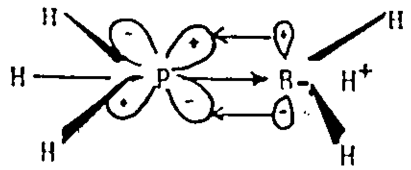


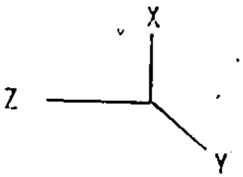
acceptor simply because its LUMO is more accessible than that of BF_3 for any given degree of distortion. But since BCl_3 is more easily reorganized as well, both factors are seen to work simultaneously to make it a better acceptor species relative to BF_3. Similar considerations might also be applied to BBr_3 and BI_3.

6. The Borane Hyperconjugative Model of P-B Bonding. The varying degrees of stability observed in addition complexes, particularly those involving phosphorus and boron, have occasioned numerous discussions

regarding the nature of bonding in these systems. Reversals in base strength have also been observed and this has influenced the development of various modular descriptions of the coordinate bond in addition compounds.

Reference has already been made to the explanation proposed by Burg[26] that the unusual oxidative and thermal stability of polymeric phosphinoboranes arises from a (2p-3d or 4p)π bonding between boron and phosphorus which is supplemental to the σ-bonding between the two. The reduced reactivity of hydrogen bonded to boron towards protonic solvents suggests a loss of hydridic character. This inertness is explained in terms of a hyperconjugative drift of charge from the B-H bond into the adjacent (p-d)π system of boron and phosphorus. A similar explanation is used in the case of the totally methylated systems $[(CH_3)_2PB(CH_3)_2]_{3,4}$. The model recently labelled the "borane hyperconjugative model"[62] has since been invoked to rationalize the unexpected stability (or existence) of certain 1:1 adducts. It has also been found useful in explaining reversals in base strength. A valence bond "resonance" picture of this condition may be envisioned as a composite of several structures of the type:





Graham and Stone[64] refer to Burg's model[76] to rationalize the existence of $CO \cdot BH_3$ and the non-existence of $CO \cdot BF_3$. In the latter compound hyperconjugation is impossible because of the heavy concentration of charge in the BF bonding system. The highly electronegative fluorine atoms do not permit drift of supplemental charge into the dative bond region. In similar fashion the existence of F_3PBF_3 and F_3NBF_3 are explained. Compatible also with borane hyperconjugation is the observation that when both BF_3 and BH_3 form complexes with ligands that can bond only by means of a σ-bond, the stabilities of their adducts are rather similar. On the other hand, when ligands possessing low energy vacant orbitals are involved, for example, Me_3P or Me_2S, the borane complexes are invariably stronger. Madden and co-workers,[77] in a comprehensive investigation of the triphenylphosphine adducts of BH_3 and BCl_3 found the hyperconjugative model compatible with observations on enthalpies of formation, dipole moments, infrared spectra, and chemical reactivity. In the latter study the borane hydrogen was found to be electropositive, as would be predicted on the basis of hyperconjugation, in two reactions. In the first,

$$Ph_3PBH_3 \quad + \quad 3\ ICl \quad \xrightarrow[25^\circ C]{CCl_4} \quad Ph_3PBI_3 \quad + \quad 3\ HCl \quad ,$$

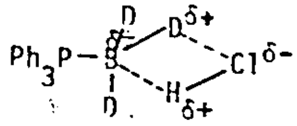
a transition state involving electropositive hydrogen is proposed:

$$\longrightarrow \quad Ph_3PBH_2I \quad + \quad HCl.$$

In the second:

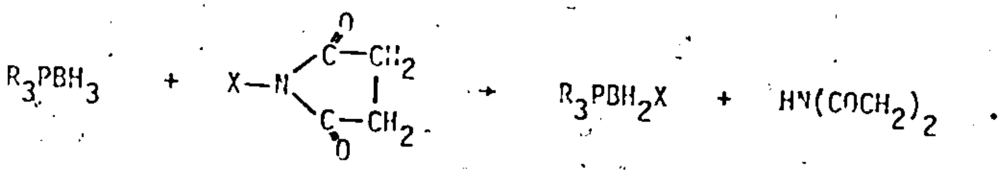
$$Ph_3PBH_3 \quad + \quad HCl \quad \xrightarrow[60^\circ C]{PhMe} \quad ,$$

the original compound was recovered intact after 48 hours. But when Ph_3PBD_3 was employed, it was found that exchange occurs even at room temperature. The proposed transition state is similar to the first:



In contrast, the borane hydrogen atoms in alkylamine boranes react as if they are hydridic, being replaced by chlorine in ICl reactions and yielding H_2 in hydrogen halide reactions.[78] Supplemental π-bonding in the alkylamine borane compounds is ruled out by the absence of low lying vacant orbitals on nitrogen.

The lability of borane hydrogen, but not of hydrogen on phosphorus, has been noted in a nuclear magnetic resonance study of the series PH_3-$BH_{3-n}X_n$ (X = Cl, Br; n = 1, 2).[79] Laurent et al.[80] have exploited the acidic character of borane hydrogen in similar adducts to successively halogenate trialkylphosphine boranes using N-halogeno-succinimide:



Acidic hydrogen on boranes has also been cited as the cause of polymerization of mixed hydride-halide adducts, $H_3PBH_{3-n}X_n$ (n = 1, 2) with the evolution of H_2.[81]

Reversals in base strength have also been explained in terms of the borane hyperconjugative model. Although this phenomenon is not unique to borane adducts* it is more pronounced. In borane adducts with fully methylated donors P > N and S > O. This is in contrast to the expected

---

*For example, toward trimethylaluminum[82] as a reference acid the order of stability of adducts of fully methylated bases is N > P and O > S > Se; toward trimethylgallium[83] the order is N > P, but O > Se > S. See also reference 35.

order as found in the BF_3 adducts.[35,[illegible]] Since phosphorus and sulfur possess the low energy vacant orbitals needed for π-bonding with borane, the complexes are stronger than are those of nitrogen and oxygen bases. With BF_3, where hyperconjugation is unlikely, the "normal" order prevails.

The notion of supplemental π-bonding in simple addition compounds was utilized by Chatt[35,84] in his formulation of Class "a" and Class "b" acceptor species. Class "b" character is thought to depend upon the availability of electrons in the acceptor for π-bonding. Thus BF_3 is characterized as an acceptor of Class "a" type, while $[BH_3]$ is said to possess mild Class "b" character. The "hard" and "soft" terminology of Pearson[85] can, of course, be applied to these acids and bases. The secondary bonding capabilities of various species are recognized. Thus the "soft acid" $[BH_3]$ is considered a potential π-donor; a "hard acid" BF_3 is thought of as a potential π-acceptor. Certain exceptions to this general treatment are mentioned, and in a recent review,[86] Bent speaks of the difficulties encountered when terminology is too closely tied to theoretical, and hence provisional, models.

Apparent exceptions to the hyperconjugative model have been observed. Base strength reversal has been noted for the acid $\underbrace{S(CH_2)_2}BH$ and BCl_3.[61] This latter is particularly important because of the impossibility of a B-H hyperconjugative interaction. The model has also been called into question through the fluorophosphine work of Rudolph and Parry.[87] F_3P would be expected to behave as a better π-acceptor toward $[BH_3]$ than F_2HP, since the former has more electron-withdrawing groups attached to phosphorus. It is found however that $[BH_3]$ forms stronger adducts with F_2HP.

A recent review on outer d-orbital bonding re-examines the π-back bonding model relative to the stability of phosphinoboranes.[88] A re-interpretation of the structural evidence, bond angles and bond lengths, for $(Me_2PBH_2)_3$[32] and $(Me_2PBH_2)_4$[31] indicates that these molecules possess a basic structure with little substantial double bonding. The high stabilities of the polymers are thought to be inconsistent with the requisite B-H bond weakening concomitant with hyperconjugation. Infrared data does not reveal significant B-H bond weakening. The high degree of stability of these compounds is instead ascribed to a kinetically controlled condition. The known steric crowding of the exo-cyclic groups hinders chemical attack, thereby engendering a high potential barrier between reactant and product species.[88]

The results of a recent ^{11}B-^{1}H n.m.r. investigation on phosphine borane adducts can be interpreted without recourse to the hyperconjugation hypothesis.[62] The results of SCF-MO calculations indicate that d-orbital participation and π-back donation play only a very minimal role in the coordinate bonding in PH_3BH_3[89] and PH_3BF_3.[90] Moreover Muetterties has also observed that a simpler and perhaps more economical explanation for the atypical bonding properties of $[BH_3]$ as compared to BF_3 and other boron trihalides is to be seen in the fact that the σ-overlap integrals in $CO \cdot BH_3$ and F_3PBH_3 are greater than in the hypothetical $CO \cdot BF_3$ and F_3PBF_3.[91]

7. The σ-Bonding Model of P-B Bonding. The apparent inadequacies of the hyperconjugative model of P-B bonding in phosphine boranes have led to the formulation of an alternative description. Rudolph, Parry and co-workers[87,92,93] have proposed a theory of P-B bonding without recourse to π-back bonding arguments. The "σ-bonding model" relates the strength of the donor-acceptor interaction to the intensity of the positive field generated at the boron kernel and to two properties of the Lewis base: (a) the dipole moment and (b) the polarizability of the lone electron pair.

The underlying principle in this conceptualization is that any property of acid or base which promotes a close approach of the positive bonding site of the one to the electron cloud of the other will favor a strengthened interaction.

In the planar BX_3 acids the symmetrical arrangement of groups attached to boron effectively reduces any localization of positive charge on boron. When the molecular species undergoes rearrangement to a pseudo-tetrahedral configuration, the system becomes quite polar with a significantly positive site at boron. The effectiveness with which this process occurs depends upon two factors. The first is extrinsic to the system and is merely a function of the proximity of approach between acid and base. The intrinsic factor, already discussed in some detail, is the ease with which the acid molecule undergoes deformation. The nature of the groups attached to boron determines the relative ease with which reorganization occurs. For example, when X is fluorine a large energy expenditure is required to produce deformation; this inhibits the formation of a strong positive field at boron. On the other hand, when X is hydrogen the initial energy requirement is less and a better condition exists for ultimate bond formation.

As pointed out above, the external factor controlling the generation of a strong field at boron is the closeness with which the electron pair on the donor can come to the potential bonding site. (This concept is not far removed from one of the basic ideas of the Mullikan theory cited earlier.[40]) In phosphine the donor orbital is largely "s" in character; the electrons are rather tightly held relative to what is observed in alkyl phosphines. This makes for a low degree of polarizability and a low dipole moment (μ_{PH_3} = 0.578±0.010;[94] μ_{MePH_2} = 1.100±0.010 D[95]). These conditions tend to make phosphine a poor coordinating agent even in those circumstances where a positive field on boron is generated with relative ease, as in [BH_3].

The electron-pair on nitrogen in ammonia on the other hand has far more directional character than it does on phosphine. Unlike the latter, ammonia approaches sp^3 hybridization in the ground state; hence the additional p-character in the lone electron pair orbital. A dipole moment of 1.47 D[96] reflects this condition. It is interesting to note at this point that the dipole moments of methylated amines fall from 1.47 D in ammonia to 0.61 D in Me_3N.[96] The opposite trend is observed in the phosphine analogues where μ ranges form 0.58 D in PH_3[94,96] to 1.19 D in Me_3P.[96] Here is a factor which may conceivably play an important role in the base strength reversals previously noted and which were satisfactorily explained by the hyperconjugative model. To reiterate, in borane adducts with fully methylated donors P > N and S > O as donor atoms.

A substitution of hydrogen by methyl groups on PH_3 increases the dipole moment and the polarizability of the ligand thereby enhancing the strength of the P-B σ-bond; a substitution of hydrogen by more electronegative species would be expected to produce opposite effects. In actual fact the order of basicity of fluorophosphines toward $[BH_3]$ is observed to be $PF_2H > PF_3 > PH_3$.[87] That PF_3 is a stronger base than PH_3 is explained on the basis of its ability (unlike the latter) to bond at unusually short bond distances. Thus F_3PBH_3 exhibits a weak, yet relatively short bond (1.836 Å).[97] The weaker, longer bond in PH_3BH_3 is 1.93 Å.[23] The electron pair on the difluorophosphine ligand is held more loosely than in the fully fluorinated compound and hence tends to form a stronger P-B bond with $[BH_3]$ (bond distance, 1.832 Å).[98] The non-existence of F_3PBF_3 and F_3NBF_3 is explained on the basis of the high re-organization energy of the acid.

The explanation for the observed order of fluorophosphine basicity toward $[BH_3]$ is not accomplished without difficulty and may point to some inadequacy in the σ-bonding hypothesis of P-B bonding. No doubt the factors which accompany dative bond formation in phosphine boranes are many and complex. It is interesting to note however that the two theories briefly surveyed above were formulated mostly on the basis of data obtained from Lewis base adducts of $[BH_3]$. In the work which follows, data of various types, ^{1}H, ^{11}B, ^{31}P, ^{19}F, nuclear magnetic resonance, and vibrational spectroscopic, have been gathered on several BX_3 (simple and mixed) adducts of phosphine and its derivatives, both alkyl and aryl. With the wider perspective afforded by this material, some indication may be obtained as to the best direction to follow in further testing of existing theory.

REFERENCES

1. H. S. Booth and D. R. Martin, "Boron Trifluoride and Its Derivatives," John Wiley and Sons, Inc., New York, 1949
2. N. N. Greenwood and R. L. Martin, Quart. Revs., 8, 1 (1954).
3. D. R. Martin, Chem. Revs., 34, 461 (1944).
4. D. R. Martin, ibid., 42, 581 (1948).
5. F. G. A. Stone, Quart. Revs., 9, 174 (1955).
6. H. I. Schlesinger and A. B. Burg, Chem. Revs., 31, 1 (1942).
7. M. F. Lappert, ibid., 56, 959 (1956).
8. F. G. A. Stone, ibid., 58, 101 (1958).
9. H. Davy, Phil. Trans., 30, 365 (1812).
10. A. Besson, Compt. Rend. Acad. Sci. Paris, 110, 516 (1890).
11. G. N. Lewis, J. Amer. Chem. Soc., 38, 762 (1916).
12. G. N. Lewis, "Valence and the Structure of Atoms and Molecules," ACS Monograph Series, Chemical Catalog Co., Inc., New York, 1923, p. 141.
13. E. L. Gamble and P. Gilmont, J. Amer. Chem. Soc., 62, 717 (1940).
14. H. I. Schlesinger and A. B. Burg, ibid., 60, 290 (1938).
15. H. I. Schlesinger, R. J. Sanderson, and A. B. Burg, ibid., 61, 536 (1939); 62, 3421 (1940); A. B. Burg ~~and H. I. Schlesinger~~, ibid., 62, 3425 (1940); H. I. Schlesinger and H. C. Brown, ibid., 62, 3429 (1940).
16. A. B. Burg, ibid., 69, 747 (1947).
17. S. G. Shore and R. W. Parry, ibid., 80, 8 (1958); 80, 12 (1958); R. C. Taylor, D. R. Schultz, and A. R. Emery, ibid., 80, 27 (1958).
18 H. Brumberger and R. A. Marcus, J. Chem. Phys., 24, 741 (1956).
19. E. L. McGandy, Diss. Abst., 22, 754 (1961).
20. R. W. Rudolph, R. W. Parry, and C. F. Farran, Inorg. Chem., 5, 723 (1966).

21. J. Davis and J. E. Drake, J. Chem. Soc., (A), 2959 (1970). A study parallel to that of Rudolph et al. was carried out by W. Sawodny and J. Goubeau, Z. anorg. allgem. Chemie, 356, 289 (1967).
22. J. E. Drake and J. Simpson, J. Chem. Soc., (A), 974 (1968).
23. J. R. Durig, Y. S. Li, L. A. Carreira, and J. D. Odom, J. Amer. Chem. Soc., 95, 2491 (1973).
24. A. Stock and E. Pohland, Chem. Ber., 59, 2215 (1926).
25. S. H. Bauer, Chem. Revs., 31, 43 (1942).
26. H. I. Schlesinger and A. B. Burg, ibid., 31, 1 (1942).
27. E. Wiber, K. Hertwig, and A. Bolz, Z. anor. allgem. Chemie, 255, 141 (1947); 256, 177 (1948).
28. E. Wiberg, Naturwissenschaften, 35, 182, 212 (1948).
29. A. B. Burg and R. I. Wagner, J. Amer. Chem. Soc., 75, 3872 (1953); A. B. Burg, Rec. Chem. Prog., 15, 159 (1954).
30. R. C. Vickery, Nature, 184, 268 (1959).
31. P. Goldstein and R. A. Jacobson, J. Amer. Chem. Soc., 84, 2457 (1962).
32. W. C. Hamilton, Acta Cryst., 8, 199 (1955).
33. H. A. Skinner and N. B. Smith, J. Chem. Soc., 4025 (1953).
34. E. R. Van Artsdalen and A. S. Dworkin, J. Amer. Chem. Soc., 74, 3401 (1952).
35. S. Ahrland, J. Chatt, and N. R. Davis, Quart. Revs., 12, 265 (1958); A. B. Burg, J. Chem. Educ., 37, 482 (1960).
36. S. H. Bauer, J. Amer. Chem. Soc., 59, 1804 (1937).
37. S. H. Bauer, ibid., 60, 524 (1938).
38. P. S. Bryan and R. L. Kuczkowski, Inorg. Chem., 11, 553 (1972).
39. F. Gallais, P. de Loth, and J. P. Labarre, Compt. Rend. Acad. Sci. Paris, C265, 363 (1967).
40. R. S. Mullikan, J. Amer. Chem. Soc., 74, 811 (1952).
41. J. N. Murrell, S. F. A. Kettle, and J. M. Tedder, "Valence Theory," John Wiley and Sons, Inc., New York, 1965, pp. 332 ff.

42. R. Foster, "Organic Charge-Transfer Complexes," Academic Press, New York, 1969, pp. 23 ff.

43. G. B. Kistiakowski and R. Williams, *J. Chem. Phys.*, *23*, 334 (1955).

44. J. N. Murrell, *J. Amer. Chem. Soc.*, *81*, 5037 (1959).

45. M. R. J. Dack, *J. Chem. Educ.*, *50*, 169 (1973).

46. C. A. Coulson, "Valence" 3rd Edition, Clarendon Press, Oxford, 1961, p. 129.

47. M. J. S. Dewer and A. R. Lepley, *J. Amer. Chem. Soc.*, *83*, 4560 (1961).

48. G. Briegleb, "Electron-Donator-Acceptor Komplexe" Springer-Verlag, Berlin, 1961.

49. M. Rabinovitz and A. Grinvald, *J. Amer. Chem. Soc.*, *94*, 2724 (1972).

50. D. P. N. Satchell and R. S. Satchell, *Chem. Revs.*, *69*, 251 (1969).

51. G. N. Lewis, *J. Franklin Inst.*, *226*, 293 (1938).

52. (a) H. C. Brown, M. D. Taylor, and M. Gerstein, *J. Amer. Chem. Soc.*, *66*, 431 (1944); (b) H. C. Brown, H. Bartholomey, and M. D. Taylor, *ibid.*, *66*, 435, (1944); H. C. Brown and M. Gerstein, *ibid.*, *72*, 2923 (1950).

53. S. Sujishi, *Diss. Abstr.*, *16*, 660 (1956).

54. H. C. Brown, *J. Chem. Soc.*, 1248 (1956).

55. H. C. Brown, E. A. Fletcher, E. Lawton, and S. Sujishi, *Abs., 121st National Meeting*, American Chemical Society, 1952, p. 9N.

56. D. H. Aue, H. M. Webb, and M. T. Bowers, *J. Amer. Chem. Soc.*, *94*, 4726 (1972).

57. J. B. Briggs, R. Yamdegni, and P. Kebarle, *ibid.*, *94*, 5129 (1972).

58. M. Munson, *ibid.*, *87*, 2332 (1965).

59. E. M. Arnelt, *ibid.*, *94*, 4724 (1972).

60. I. Dzidic, *ibid.*, *94*, 8333 (1972).

61. D. E. Young, G. E. McAchran, and S. G. Shore, *ibid.*, *88*, 4390 (1966).

62. A. H. Cowley and M. C. Damasco, *ibid.*, *93*, 6815 (1971).

63. R. Foester and K. Cohn, *Inorg. Chem.*, *11*, 2590 (1972).

64. W. A. G. Graham and F. G. A. Stone, J. Inorg. Nucl. Chem, 3, 164, (1956).

65. J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. II, Pergamon Press, London, 1964, p. 1109.

66. G. R. Eaton and W. N. Lipscomb, "NMR Studies of Boron Hydrides and Related Compounds," W. A. Benjamin Co., Inc., New York, 1968, pp. 542 ff.

67. H. C. Brown and R. R. Holmes, J. Amer. Chem. Soc., 78, 2173 (1956).

68. J. M. Miller and M. Onyschuk, Canad. J. Chem., 42, 1518 (1964).

69. F. A. Cotton and J. R. Leto, J. Chem. Phys., 30, 993 (1959).

70. T. Wentink and V. H. Tiensuu, ibid., 28, 826 (1958).

71 M. F. Lappert, M. R. Litzow, J. B. Pedley, P. N. K. Riley, and A. Tweedale, J. Chem. Soc., (A), 3105 (1968).

72. J. A. S. Smith and D. A. Tong, ibid., 173 (1971).

73. P. J. Bassett and D. R. Lloyd, ibid., 1551 (1971).

74. T. B. Eames and B. M. Hoffman, J Amer. Chem. Soc., 93, 3141 (1971).

75. D. F. Shriver and B. Swanson, Inorg. Chem., 10, 1354 (1971).

76. F. G. A. Stone and A. B. Burg, J. Amer. Chem. Soc., 76, 386 (1954).

77. M. A. Frish, H. G. Heal, H. Mackle, and I. O. Madden, J. Chem. Soc., 899, 1965.

78. H. Nöth and H. Beyer, Chem. Ber., 93, 2251 (1960).

79. J. E. Drake and J. Simpson, J. Chem. Soc., 974 (1968) and references therein.

80. G. Jugie, J. P. Laussac and J. P. Laurent, Bull. Chim. Soc. Fr., 2542 (1970).

81. J. E. Drake and J. Simpson, Inorg. Nucl. Chem. Letters, 3, 87 (1967).

82. N. Davidson and H. C. Brown, J. Amer. Chem. Soc., 64, 316 (1942).

83. G. E. Coates, J. Chem. Soc., 3003 (1951).

84. J. Chatt, Nature, 165, 637 (1950).

85. R. G. Pearson, *J. Amer. Chem. Soc.*, *85*, 3533 (1963).

86. H. A. Bent, *Chem. Revs.*, *68*, 587 (1968).

87. R. W. Rudolph and R. W. Parry, *J. Amer. Chem. Soc.*, *89*, 1621 (1967).

88. K. A. R. Mitchell, *Chem. Revs.*, *69*, 157 (1969).

89. J. Demuynck and A. Veillard, *Chem. Comm.*, 873 (1970).

90. I. H. Hillier, J. C. Marriof, V. R. Saunders, J. J. Ware and D. R. Lloyd, *ibid.*, 1586 (1970).

91. E. L. Muetterties, "The Chemistry of Boron and Its Compounds," John Wiley and Sons, Inc., New York, 1967, p. 12.

92. R. W. Rudolph and C. W. Schultz, *J. Amer. Chem. Soc.*, *93*, 6821 (1971).

93. S. Fleming and R. W. Parry, *Inorg. Chem.*, *11*, 1 (1972).

94. C. A. Barrus, *J. Chem. Phys.*, *28*, 427 (1958).

95. T. Kojima, E. Breig, and C. C. Lin, *ibid.*, *35*, 2139 (1961).

96. J. R. Weaver and R. W. Parry, *Inorg. Chem.*, *5*, 718 (1966).

97. R. L. Kucakowski and D. R. Lide, *J. Chem. Phys.*, *46*, 357 (1967).

98. J. P. Pasinski and R. L. Kuckowski, *ibid.*, *54*, 1903 (1971).

CHAPTER II

THE ^1H NUCLEAR MAGNETIC RESONANCE INVESTIGATION

INTRODUCTION

The results of the proton magnetic resonance investigation which follow pertain specifically to the ^1H n.m.r. parameters of the proton(s) directly attached to phosphorus and only incidentally to the ^1H parameters of other substituents on phosphorus. A relatively small number of donor-BX_3 studies have appeared in which ^1H n.m.r. parameters of hydrogen directly bonded to the donor are used for diagnostic purposes.[1-8] By way of contrast, the ^1H n.m.r. parameters of hydrogen in alkyl groups attached to donor atoms in boron trihalide complexes have been studied extensively in the years since Diehl and Ogg reported a downfield displacement in the proton resonance shifts of ethanol upon complexation with BF_3 and BCl_3.[9,10] The relevance of this material to the present investigation lies in the diagnostic value of the data relative to Lewis acid-base strengths and complex stabilities. Consequently, a brief survey of this literature seems appropriate.

A wide variety of alkyl-containing Lewis bases has been employed in complexation reactions with both simple and mixed boron trihalide species. Regardless of the donor used, however, complexation invariably results in a proton resonance shift to lower field strengths.

1. Nitrogen Donors. Massay and Park, as part of an investigation into the properties of tris(pentafluorophenyl) boron, used trimethylamine to evaluate the relative acid strengths of several boron acceptors.[11] On

the premise that withdrawal of electron density from the donor moiety would be expected to result in a methyl proton deshielding, the strengths of the various acids were correlated with the magnitude of downfield shift exhibited by the methyl resonance upon adduct formation. The order of decreasing acidity was given as: $BI_3 > BBr_3 > BCl_3 > B(C_6F_5)_3 = BF_3 = [BH_3] > BMe_3$. This ordering was found to be in general agreement with the results of a previous investigation in which the n.m.r. parameters of the boron trihalide-trimethylamine adducts in chloroform solvent had been correlated with adduct dipole moments and heats of formation.[12] In the latter study $[BH_3]$ was found to be a slightly stronger acid than BF_3. Furthermore, the methyl resonance in the Me_3N adducts of BBr_3 and BCl_3 appeared as a closely spaced 1:1:1:1 quartet, but only as a singlet in the other two adducts. This splitting was also observed by another group[13] and attributed to an indirect nitrogen-hydrogen coupling, J_{NCH}. This would be expected to yield a triplet ($I_{^{14}N} = 1$) rather than a quartet, however; the quartet has since been attributed to long-range boron-hydrogen coupling, J_{BNCH}.[14] This indirect coupling has also been observed for the dimeric species $(Me_2NBF_2)_2$.[15] Rademaker and Ryschkewitsch[16] have observed the long-range spin-spin coupling between H and B when boron is tetrahedral and exclusively connected to nitrogen, chlorine or bromine. They did not observe the coupling when H or F was a substituent on boron.

Coyle and Stone, in their study of this adduct series in methylene chloride,[17] found BF_3 to be somewhat more acidic than $[BH_3]$ contrary to the findings of Onyszchuk and Miller;[12] but the discrepancy, being small, is attributable to solvent effects.

Trimethylamine has also been used as a reference base in evaluating the relative strengths of a series of 14 mixed boron trihalide acids.[18] In their order of decreasing acidity, the acids are listed as $BI_3 > BClI_2 > BBr_3 > BCl_2I > BClBr_2 > BCl_2Br > BFI_2 > BCl_3 > BFBr_2 > BFCl_2 > BF_2I > BF_2Br > BF_2Cl > BF_3$.* The methyl resonance varies from - 3.18 ppm for the BI_3 adduct to - 2.58 ppm for the BF_3 adduct, with that of the pure base given as - 2.20 ppm relative to tetramethylsilane, TMS.

In another study involving acetonitrile as the reference base[20] the downfield shift of the methyl proton resonance was correlated with the acidity order: $BI_3 > BBr_3 > BCl_3 > BF_3$. Here also chemical shifts were found to linearly correlate with adduct dipole moments and heats of formation. The chemical shift values of the trimethylamine and acetonitrile systems, converted from the cps to the ppm scale, are presented in Table II - 1. As might be expected, the downfield complexation shift is more pronounced for hydrogen attached to a carbon α to the donating group than it is if further removed. This was also observed in the spectra of the BX_3 adducts of triethylamine but it was not found possible to correlate the difference in methyl and methylene chemical shifts with adduct stability or Lewis acidity.[17]

2. Oxygen Donors. Dimethyl ether has recently been employed as a reference base in a nuclear magnetic resonance study of its adducts with mixed boron trihalides in methylene chloride solution.[21] ^1H n.m.r.

---

*A more extensive listing of acid strength involving some 20 boron trihalide acids including four triple-mixed species: BClBrI, BFBrI, BFClI, and BFClBr, has since been published by the same authors. This second study involved the use of both Me_3N and 4-methylpyridine as reference bases.[19]

TABLE II - 1

^{1}H n.m.r. chemical shifts in ppm of the methyl protons in the BX_3 (X = H, F, Cl, Br, I) adducts of trimethylamine and acetonitrile.

	Me_3N (in $CHCl_3$)	Me_3N (in $PhNO_2$)	MeCN (in $PhNO_2$)
Free Base	-2.20		-2.10
$[BH_3]$	-2.65		
BF_3	-2.62	-2.76	-2.69
BCl_3	-3.00	-3.12	-3.05
BBr_3	-3.18	-3.23	-3.17
BI_3	-3.35		

chemical shifts of the mixed halogen species are found to be intermediate between those of the corresponding unmixed halogen species. The order of decreasing acidity given in terms of δ_{CH_3} is: $BI_3 > BBr_3 > BClBr_2 > BCl_2Br > BCl_3 > BFBr_2 > BFClBr > BFCl_2 > BF_2Br > BF_2Cl > BF_3$. There is no reversal in strength to be noted in this series as compared to that observed when trimethylamine was used as the reference base. The triple mixed boron halide, BFClBr, is observed to interpolate between $BFBr_2$ and $BFCl_2$. The chemical shifts of the methyl protons on the mixed species range from -4.46 ppm (Me_2OBI_3) to -3.96 ppm (Me_2OBF_3) with that of the free base in CH_2Cl_2 given as -3.38 relative to TMS.

Several investigations involving reactions of boron acids with simple[17,22,23] and cyclic ethers[24] have been reported. While the expected correlation between chemical shift and boron halide acidity is observed, the effects on chemical shift from steric hindrance in bulky systems or from bond anisotropy are noted.[22,23] Furthermore, a word of caution is injected relative to interpreting chemical shift changes solely in terms of changes in electron density on hydrogen. Nevertheless, for the simple ether systems some interesting correlations are found. Unlike the previously cited triethylamine study,[17] it is noted that in the 1:1 BX_3 adducts of diethylether differences between methyl and methylene proton resonances correlate with acid strength: BBr_3 ($\Delta\delta$ = 59 Hz) > BCl_3 ($\Delta\delta$ = 55 Hz) > BF_3 ($\Delta\delta$ = 39 Hz).[22] The differing extents of methyl and methylene shifts had been previously noted by Craig and Richards[25] for ether systems and by Gillespie and Hartman[26] for ketone adducts with BX_3 species, but no correlation was attempted.

N,N-Dimethylforamide has been used as a complexing base for a wide variety of Lewis acids including transition element compounds as well as compounds of Groups III, IV, and V.[27] The restricted rotation about the C-N bond at low temperature permitted the ordering of acidities in terms of resonance shifts of both cis and trans methyl groups.

That the attack of the acid species (specifically, BX_3 moieties) occurs at oxygen in amides and oximes has been substantiated by Lappert and co-workers.[28,29]

3. Other Donors. A recent exchange study[30] of BX_3 adducts of Me_2S reports parenthetically the methyl proton resonance positions of the BI_3 adduct through the BF_3 adduct as -2.65, -2.64, -2.58, and -2.40 ppm, respectively at -93°C, relative to TMS. The methyl proton resonance of the reference base on the same conditions is -2.14 ppm. These results

are in accord with the observations made in other systems. A ^1H and ^{11}B study of BX_3 adducts of the reference bases R_2E (R = Me, Et, iso-Pr; E = S, Se, Te) has recently been reported.[31] In all cases proton resonances are seen to move downfield with increasing acidity of the acceptor species.

In the following investigation, the ^1H n.m.r. parameters are those of hydrogen directly connected to the donor atom. As such, the chemical shift difference ($\Delta\delta = \delta_{ligand} - \delta_{adduct}$) on complexation should be of greater magnitude than in the alkyl-substituted donors. Furthermore, the chemical shift might be expected to be more responsive to subtle variations in the donor-acceptor interaction as a function of changes on either moiety. Since phosphorus is the donor atom ($I_{^{31}P} = \frac{1}{2}$), the pronounced P-H spin-spin coupling should also be of significant advantage in assessing acid-base strengths and complex stabilities.

EXPERIMENTAL

All adducts except for $PhPH_2BI_3$ and Ph_2PHBI_3 were prepared by direct combination of reactants in reaction vessels D and E on the vacuum line. Deuterated methyl phosphines were employed in order to avoid the ^1H n.m.r. methyl resonance which occurs in very close proximity to the upfield resonance peak of the PH doublets.

1. The Formation of the Adducts $(CD_3)_nPH_{3-n}BX_3$ (n = 0, 1, 2; X = H, F, Cl, Br). Equimolar quantities (usually ca. 0.5 mmole) of the donor species and the appropriate Lewis acid (0.25 mmole for B_2H_6) were distilled into evacuated vessel D at -196°C. As the contents were allowed

to slowly warm to room temperature, the formation of a white, solid material ensued. (In the case of the B_2H_6 reactions, the adducts were often clear liquids. The warm-up was not allowed to proceed beyond -20°C. Rapid warming to room temperature resulted in the formation of a solid polymeric species[32] and 1:1 adduct. The same procedure was followed relative to the BF_3 adducts because of their instability with respect to dissociation.)

After 1 hour at the specified temperature the vessel was opened momentarily to the vacuum line to remove excess of either reactant. The CD_3I (ca. 5 mmole)* and a trace of tetramethylsilane were distilled on to the product at -196°C. The tube was then sealed.

2. The Formation of the Adducts $(CD_3)_nPH_{3-n}BI_3$ (n = 0, 1, 2). Boron triiodide, in appropriate molar quantity, was purified by agitating a benzene solution of the compound with a trace of elemental mercury in a closed vessel under moisture-free conditions. The solution was then decanted in a dry box to vessel E. The contents were frozen, the vessel attached to the vacuum line and evacuated, and the requisite base distilled into the tube. Upon warming and off-line agitation, the appearance of a fine white precipitate indicated adduct formation. With the vessel back on the vacuum line and the contents at -78°C the tube was opened to the manometer. A slight positive pressure indicated excess phosphine donor which was then pumped away. The benzene was carefully

---

*Use of CD_3I as solvent for the $(CD_3)_nPH_{3-n}BX_3$ (n = 1, 2) had to be abandoned because of its tendency to solidify in the presence of these adducts at temperatures as high as -40°C. CH_2Cl_2 was found to be a suitable solvent for these systems, whereas its utility was severely limited in the PH_3BX_3 system.

removed by vacuum distillation; solvent and TMS were added and the tube was sealed.

3. The Formation of the Adducts $Ph_nPH_{3-n}BX_3$ (n = 1, 2; X = H, F, Cl, Br). The low vapor pressures of both phenylphosphines made vacuum line manipulation inefficient. Consequently, a measured quantity of either material (ca. 0.5 mmole) was transferred to Vessel E under moisture-free conditions by means of a microliter syringe. Requisite volumes were calculated on the basis of literature values for the densities of phenylphosphine, d_{16} = 1.01 g/cc,[33] and diphenylphosphine, d_{16} = 1.07 g/cc.[34] Except in the preparation of the BF_3 adducts, a small quantity of benzene was added to the tube prior to attachment to the vacuum system. The solution was then frozen, the tube evacuated, and a measured excess of BX_3 added. Upon warming and agitation the adduct formed as a white precipitate. (In the absence of benzene, reactions occasionally exhibited considerable localized heating accompanied by formation of yellow or orange products. Benzene was omitted in the preparation of the $[BH_3]$ adducts where B_2H_6 and the appropriate phosphine were allowed to react directly at 0°C.) The benzene was distilled off and additional BX_3 was admitted to ensure completeness of reaction. After 1 hour the tube was evacuated and, except for the BF_3 and $[BH_3]$ systems, was opened to the pump for 15 min. Solvent and TMS were added and the tube was sealed.

4. The Formation of $Ph_nPH_{3-n}BI_3$ (n = 1, 2). A measured quantity of the required phosphine in slight excess was introduced into vessel E under moisture-free conditions. Benzene was added, followed by the addition of a benzene solution of purified BI_3 in approximately known molar quantity.

The unmixed system was frozen, the tube evacuated and the reactants were allowed to mix at as low a temperature as possible. After removal of benzene, the adduct was opened to the pump over night. Solvent and TMS were added and the tube was sealed.

When not in use, samples of all adducts were stored at -78°C. A considerable amount of evidence accumulated in the course of this investigation indicates that at temperatures higher than -78°C, kinetic processes involving the making and breaking of the donor-acceptor bond take place. Hence, there is likelihood of some free base being constantly present and available for reaction with the solvent. This was observed when samples were kept at room temperature for some hours, resulting in the formation of a yellow solid. The compound may be a quaternary phosphonium salt similar to the analogous ammonium salt formed by reaction of ethyldimethylamine with CH_2Cl_2.[35] Uncomplexed BI_3 will react with tetramethylsilane to give Me_3SiI as one of the products.[30]

RESULTS AND DISCUSSION

The ^1H n.m.r. investigation of each adduct was conducted over a uniformly varied temperature range from -70°C to room temperature. When adduct characteristics warranted, spectra were also recorded at higher temperatures. The complete listing of ^1H n.m.r. parameters over the entire temperature range is tabulated for each adduct series in Section 2A of the APPENDIX. The ^1H n.m.r. parameters for all five series of adducts at -70°C are displayed in Table II - 2.

TABLE II - 2

Observed ^{1}H n.m.r. parameters (δ in p.p.m. ± 0.05 p.p.m. downfield from int. TMS; J_{PH} in Hz ± 2 Hz for the boron trihalide adducts of PH_3, $(CD_3)_nPH_{3-n}$, Ph_nPH_{3-n} (n = 1, 2) recorded at -70°C in CD_3I.

	PH_3		CD_3PH_2		$(CD_3)_2PH$		$PhPH_2$		Ph_2PH	
	δ	J_{PH}	δ	J_{PH}	δ	J_{PH}	δ	J_{PH}	δ	J_{PH}
free ligand[a]	-2.02	187	-2.64	188	-3.12	191	-4.01	201	-5.44	218
$[BH_3]$	-4.31	372[b]	-4.58	375[c]	-4.78	369[d]	-5.65	375*	-6.40	381†
BF_3	-	-	-4.28	355	-4.80	384	-5.30	324(?)	-6.50	389
BCl_3	-5.92	426	-5.30	428	-5.20	420	-6.45	420	-6.80	422
BBr_3	-6.44	429	-5.60	430	-5.40	429	-6.80	430	-7.00	435
BI_3	-7.40	432	-6.20	434	-5.45	432	-7.45	434	-7.60	441

a) ^{1}H n.m.r. parameters of free ligands: PH_3, ref 36; $MePH_2$ and Me_2PH, ref 37; Ph_2PH, ref 38.

b) Ref 2; recorded at 35°C, neat.

c) Ref 8; recorded at 35°C, neat.

d) Ref 39; J_{PH} = 370; no value for δ given.

* δ_{Ph} = -7.50; J_{BH} = 103.5

† δ_{Ph} = -7.40; J_{BH} = 99.5

5

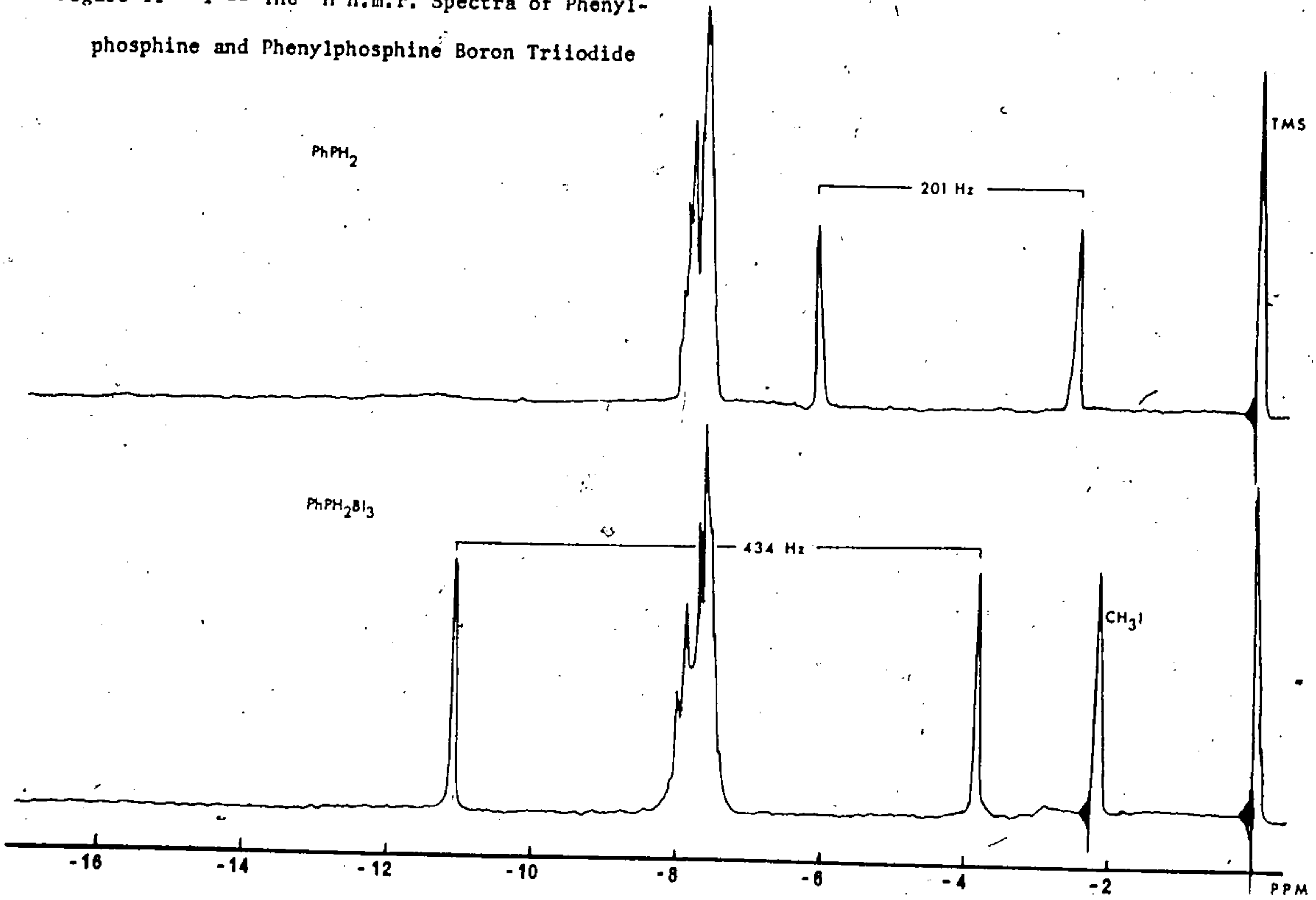
1. Chemical Shift and Acid Strength. The general trend of the chemical shift within any of the five groups upon complexation is to lower field (Table II - 2; Figure II - 1). This is consistent with what has been reported in the previously cited n.m.r. studies of proton resonances in alkyl groups attached to donor atoms. The shielding of the proton on phosphorus increases as the apparent strength of the Lewis acid decreases in accord with the generally accepted order: $BI_3 > BBr_3 > BCl_3 > [BH_3] > BF_3$. As expected, the magnitude of the change in proton resonance position from free to complexed donor is significantly larger than the corresponding change in alkyl-substituted donors.* Whereas in the latter $\Delta\delta$ varies by no more than 1.2 p.p.m. (Table II - 1), in the phosphine complexes $\Delta\delta$ can be as large as 5.5 p.p.m. (as in PH_3BI_3). The smallest value for $\Delta\delta$ in these complexes is approximately 1 p.p.m. (Ph_2PHBH_3).

A careful examination of the table will reveal the same irregularities between ^1H n.m.r. parameters of the $[BH_3]$ and BF_3 complexes as have been observed by others while investigating alkyl-substituted donors and to which attention has already be given.[12,17] Aside from these discrepancies, however, the ordered downfield trend in chemical shift within any of the five series does seem to be a moderately effective indicator of acceptor strength. Employing the conceptual model of Rudolph and Parry,[3] the increased deshielding of the phosphorus protons indicates a drift of charge to an increasingly positive center, namely, the boron kernel. The extent to which the boron kernel projects

---

*The ^1H chemical shift for protons on alkyl groups attached to four-coordinate phosphorus ranges from -2.1 to -3.3 p.p.m.; on three-coordinate phosphorus the range is from -0.9 to -2.2 p.p.m. None of the four-coordinate compounds for which values are given are adducts of the type considered here.[40]

Figure II - 1 -- The ^{1}H n.m.r. Spectra of Phenylphosphine and Phenylphosphine Boron Triiodide



a positive field is dependent upon the ease with which the BX_3 species undergoes deformation. In BI_3 deformation is most readily achieved since the planar structure is least stabilized by back-bonding. For this reason and others arising out of molecular orbital considerations, BI_3 has the greatest electron affinity of the boron trihalides and consequently has the greatest deshielding effect on protons attached to the donor moiety. BF_3, because of its relatively strong (p-p)π supplemental bonding and higher unoccupied molecular orbital exhibits weak acceptor power.

The possibility of the localization of charge on phosphorus or within the P-B bond must be examined by means of ^{31}P or ^{11}B n.m.r.

2. Chemical Shift and Base Strength. An examination of the changes in chemical shift for the entire series of adducts upon methyl- or phenyl-substitution at phosphorus reveals no obvious general trend. For Me_nPH_{3-n} adducts of any BX_3 (X = Cl, Br, I) there is greater shielding of the phosphorus proton with increasing methyl substitution. The reverse is true for Me_nPH_{3-n} adducts of $[BH_3]$ and BF_3. When Ph_nPH_{3-n} is employed in adduct formation there is a greater deshielding of the phosphorus protons with increasing phenyl substitution for all BX_3 species. The notable variance between δ-values for the $Me_nPH_{3-n}BX_3$ and $Ph_nPH_{3-n}BX_3$ adducts (X = Cl, Br, I) may, in some measure, be attributable to the deshielding effects of ring currents induced in the phenyl group by the imposed magnetic field.[41,42] This effect, together with the opposing trends noted above in the case of methyl substitution, rules out the use of chemical shift values in a predictive capacity as indicators of

relative base strength.

3. The Phosphorus-Hydrogen Coupling Constant and Acid Strength. The sensitivity of the direct coupling constant, J_{PH}, to changes in the hybridization state of phosphorus-hydrogen bonding orbitals is dramatically illustrated in the series PH_2^-, PH_3, and PH_4^+. The corresponding J_{PH} values are 138 - 140 Hz, 182 - 192 Hz, and 548 Hz (depending on the solvent used) while the hybridization states are $\sim p^2$, $\sim p^3$, and sp^3, respectively.[43] Gutowsky and co-workers have suggested that the magnitude of coupling constants between hydrogen and other directly bonded nuclei should depend significantly upon the extent of s-character of the bonding orbitals.[44] Hence large changes in J_{PH} can be related to changes in the s-character of the phosphorus-hydrogen bonding orbitals. It is reasonable to expect that in the boron trihalide adducts of the various phosphines the magnitude of J_{PH} can, therefore, be taken as a measure of s-character in the orbitals around phosphorus. The change in the magnitude of J_{PH} upon complexation of trivalent phosphorus becomes immediately obvious on comparing the ^1H n.m.r. spectrum of phenylphosphine with that of its 1:1 BI_3 adduct (Figure II - 1).

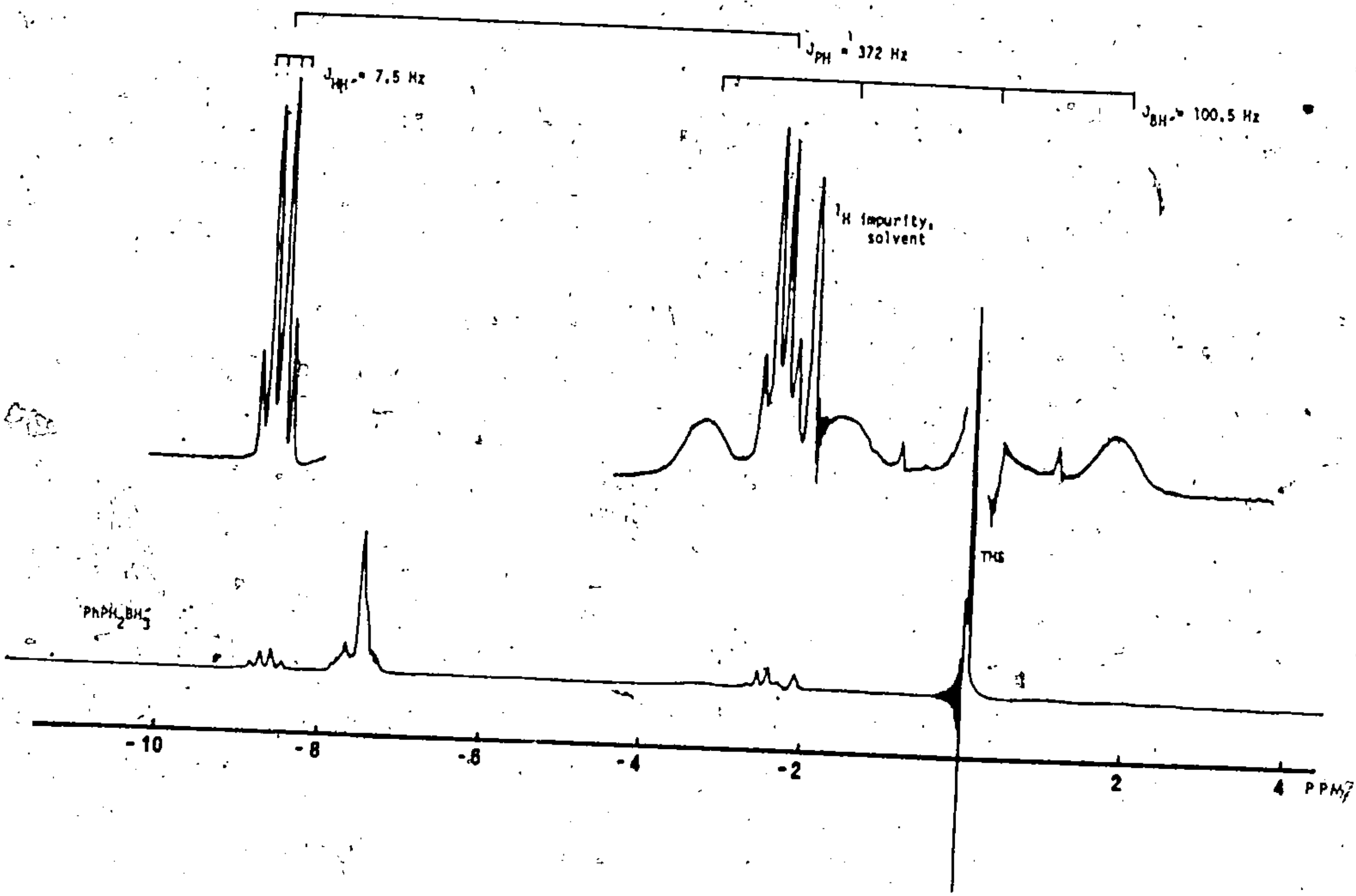
An examination of Table II - 2 will reveal that within any given donor series, variation of the Lewis acid clearly exhibits a trend in J_{PH} which suggests that the degree of s-character in the phosphorus-hydrogen orbitals increases with increasing acidity of the acceptor species. This is analogous to observations in terms of $J_{^{13}CH}$ where its value is seen to increase as the electronegativity of the moiety attached to carbon increases.[45] The trend is also in agreement with Walsh's rule that s-character tends to concentrate in those orbitals which are directed to more electropositive groups.[4,6] Thus, for the five series investigated here, the assumption that the Fermi contact term predominates in the nuclear spin-spin interaction seems to be a reasonable one.

As a concomitant to the increase in the s-character in the P-H bonding orbitals, one must posit an increase in the p-character of the phosphorus "lone-pair" orbital as it becomes involved with an increasingly electronegative boron kernel. Thus, both the chemical shift and the direct coupling constant parameters support the ordering of Lewis acidity as: $BI_3 > BBr_3 > BCl_3 > [BH_3] > BF_3$.

4. The Phosphorus-Hydrogen Coupling Constant and Base Strength. As is evident from Table II - 2, a systematic variation of Lewis bases relative to any boron acid does not reveal any distinct trend in coupling constant values. Thus, while the ^1H n.m.r. parameters may have a diagnostic value relative to estimating Lewis acidity for boron acceptors, these observables seem to exhibit little predictive value relative to base strength in the adduct series.

5. The Boron-Hydrogen Coupling Constant. The relative intensities of the proton resonance signals associated with hydrogen attached to phosphorus and hydrogen attached to boron are clearly illustrated in the ^1H n.m.r. spectrum of phenylphosphine borane in CD_3I (Figure II - 2). Because of the low intensity, wide resonance peaks of protons attached to boron, most J_{BH} parameters for adducts of the type studied here are obtained from ^{11}B n.m.r. spectra where the coupling constant can be

Figure II - 2 -- The ^1H n.m.r. Spectrum of Phenylphosphine Borane in CD_3I at 0°C.



measured more precisely. The broadening of resonance peaks is attributable to relaxation processes occurring at the boron nucleus which tend to average out the effects of the four discrete boron spin states.[47] This is not an appreciable problem with the ^1H nucleus which has no nuclear quadrupole moment to interact with fluctuating electric field gradients. Consequently the two distinct spin states of the proton are sufficiently long-lived to give satisfactorily sharp spin-spin resonance signals in the ^{11}B n.m.r. The J_{BH} values obtained from ^1H n.m.r. spectra in this investigation or from other sources are recorded in Table II - 3. The values may be compared with those obtained for the same compounds by ^{11}B n.m.r. by consulting Table IV - 4.

TABLE II - 3

The ^1H n.m.r. parameters for the proton resonance on boron in the adducts $R_nPH_{3-n}BH_3$ (R = Me, Ph; n = 0, 1, 2).

	δ	J_{BH}	Reference
B_2H_6	-3.95 p.p.m.	135 Hz	48
PH_3BH_3	-0.53	104	49
$MePH_2BH_3$	-0.53	99	8
Me_2PHBH_3	-0.50	93	this work
$PhPH_2BH_3$	-0.85	100.5	this work
Ph_2PHBH_3	-0.80	98.5	this work

The considerations applied to the relationship between s-character and the magnitude of the direct coupling constant in the phosphorus-hydrogen system should also be expected to apply to the boron-hydrogen constants. If B_2H_6 is considered as the parent compound with a terminal HBH bond angle of approximately 121^{o}[56] then it is reasonable to expect that the magnitude of J_{BH} will decrease upon adduct formation, assuming that the HBH angle now approaches 109^{o}. The data of Table II - 3 suggest that this is indeed the case.

6. The ^{1}H n.m.r. Parameters and Complex Stability. Phosphine and its derivatives react with the boron Lewis acids according to the expression:

$$R_nPH_{3-n} + BX_3 \rightleftarrows R_nPH_{3-n}BX_3 \quad .$$

The temperature of the system significantly affects the position of equilibrium relative to adduct and free reactants. If the PB bond-making bond-breaking process is rapid on the n.m.r. time scale, the resonance signals observed will be averaged values of those of the free base and of the adduct. Slowing the rate of exchange by cooling the system is reflected in corresponding changes in the the ^{1}H n.m.r. parameters. An examination of the temperature dependent ^{1}H n.m.r. data for each adduct series (Table II - 4; Appendix, Section 2A, Tables 2.1 through 2.5) will show that chemical shift and coupling constant values tend to converge to constant values as the temperature of the system is lowered. That temperature at which convergence occurs may be taken as a qualitative index of adduct stability with respect to exchange processes. The larger the temperature range over which the n.m.r. parameters remain constant, the more stable the adduct relative to dissociation. On this basis the PH_3BX_3 series could be ordered in terms of decreasing stability as: $PH_3BI_3 > PH_3BBr_3 > PH_3BCl_3 > PH_3BF_3$ (Table II - 4). Even at temperatures

TABLE II - 4

Observed ^1H n.m.r. parameters, δ_{PH} and J_{PH}, of $CD_3PH_2BF_3$[a] and PH_3BX_3[b] at various temperatures.*

	$CD_3PH_2BF_3$		PH_3BCl_3		PH_3BBr_3		PH_3BI_3	
	δ	J_{PH}	δ	J_{PH}	δ	J_{PH}	δ	J_{PH}
-70°C	-4.28	355	-5.92	426	-6.44	429	-7.40	432
-65	-4.28	350	-5.90	424	-6.44	429	-7.40	432
-40	-4.26	350	≃-5.6	≃412[c]	-6.40	428	-7.40	430
-20	-4.22	346	≃-5.7	≃400[c]	-6.34	428	-7.40	430
25	-3.72	301	-5.37	396	-6.20	424	-7.26	428

* The adduct PH_3BF_3 did not form at all at -70°C; the BF_3 adduct of Me_3PH_2 did, however. The ^1H n.m.r. parameters of this compound are included for comparison purposes.

a) Recorded in CH_2Cl_2.

b) Recorded in CD_3I.

c) Estimated values of resonance located within proton impurity peak of solvent.

as low as -70°C it was not possible to obtain nuclear magnetic resonance signals that could be interpreted as evidence for the formation of PH_3BF_3.* Similarly, the spectrum of $PhPH_2BF_3$ at -70°C is not without ambiguity, indicating that dissociation may be quite pronounced even at very low temperatures for some of the adducts.

7. The ^1H n.m.r. Parameters and Vibrational Spectroscopic Data.

Although J_{PH} values in a given adduct series seem to indicate an increase in the degree of s-character in the P-H bonding orbitals with increasing acidity of the acceptor species, chemical shift values indicate a drift of charge away from the protons, resulting perhaps in a weaker P-H bond. This seems to be indicated by the results of the vibrational spectroscopic investigation of the PH_3BX_3 (X = Cl, Br, I) system (Chapter VI). The pertinent vibrational and n.m.r. data is assembled in Table II - 5.

TABLE II - 5

Raman and ^1H n.m.r. data relative to the PH_3BX_3 (X = Cl, Br, I) adduct series

	ν_{PH} asym	ν_{PH} sym	J_{PH}
PH_3BCl_3	2447 cm^{-1}	2412 cm^{-1}	420 Hz
PH_3BBr_3	2428	2390	430
PH_3BI_3	2397	2362	436

---

*Martin and Dial reported the existence of PH_3BF_3 as a white solid at -90°C. The material was allowed to dissociate in an evacuated molecular weight bulb and measurements carried out at room temperature gave molecular weight values of approximately 1:1 phosphine to boron trifluoride.[51]

An increase in s-character with a concomitant bond weakening is not necessarily contradictory. The hybridization change in the phosphorus orbitals as suggested by the J_{PH} values of the adduct series is quite small relative to that which occurs upon adduct formation. The additional increase in s-character, and hence in orbital overlap capability, may be outweighed by a more dominant opposing factor, namely the drift of charge away from the P-H bonds toward the P-B bond. In this way the decrease in P-H stretching frequencies from PH_3BCl_3 to PH_3BI_3 as well as the increased stability of the complexes with respect to dissociation can be rationalized.

It is in observing large over-all effects that consistency between the various physical parameters is to be expected. For example, in phosphine and methylphosphine and their respective [BH_3] adducts a consistency maintains among all relevant physical parameters: bond angles, % s-character in P-H orbitals, P-H stretching frequencies, J_{PH}, and chemical shift (Table II - 6).

Thus it would seem that P-H stretching frequencies, chemical shifts and coupling constants in phosphine borane and its various derivatives reflect an inter-relation between two opposing tendencies. Bond strengthening may result as a consequence of increased overlap through greater s-participation in the hybrid bonding orbitals. Bond weakening may occur through drift of charge away from the P-H bonding orbitals.

TABLE II - 6

Various related physical parameters for phosphine, methylphosphine and their respective [BH_3] adducts

	HPH angle	% s-character†	ν_{PH} asym	ν_{PH} sym	J_{PH}	$\delta_{^1H}$
PH_3	93.3[a]	5.4	2421 cm^{-1}[d]	2327 cm^{-1}[d]	182 Hz[h]	-2.02[h]
PH_3BH_3	101.3[b]	15.2	2426[e]	2363[e]	372 [e]	-4.31[e]
$MePH_2$	93.4[c]	5.5	2310[f]	2304[f]	186[i]	-2.64[i]
$MePH_2BH_3$	99.9[c]	14.7	2306[g]	2360[g]	375[g]	-4.58[g]

† Bond angle data, when used in the Coulson relationship,[52] $1 + \lambda^2 \cos \theta = 0$, permits the calculation of the percentage s-character (λ) in a given bond (APPENDIX, Section 2B).

a) Ref. 53
b) Ref. 54
c) Ref. 55
d) Ref. 56
e) Ref. 2
f) Ref. 57
g) Ref. 8
h) Ref. 36
i) Ref. 37

REFERENCES

1. J. N. Shoolery, Disc. Faraday Soc., 19, 215 (1955).
2. R. W. Rudolph, R. W. Parry, and C. F. Farran, Inorg. Chem., 5, 723 (1966).
3. R. W. Rudolph and R. W. Parry, J. Amer. Chem. Soc., 89, 1621 (1967).
4. J. E. Drake and J. Simpson, Inorg. Nucl. Chem. Letters, 3, 87 (1967).
5. J. E. Drake and J. Simpson, J. Chem. Soc., (A), 974 (1968).
6. G. Jugie, J. P. Pouyanne, and J. P. Laurent, Compt. Rend. Sc. Paris, 268C, 1377 (1969).
7. J. Davis, J. E. Drake, and N. Goddard, J. Chem. Soc. (A), 2962 (1970).
8. J. Davis and J. E. Drake, ibid., 2094 (1971).
9. P. Diehl and R. A. Ogg, Nature, 180, 1114 (1957).
10. P. Diehl, Helv. physic. Acta, 31, 685 (1958); R. A. Ogg and P. Diehl, J. Inorg. Nucl. Chem., 8, 468 (1958).
11. A. G. Massay and A. J. Park, J. Organomet. Chem., 5, 218 (1966).
12. J. M. Miller and M. Onyszchuk, Canad. J. Chem., 42, 1518 (1964).
13. O. Ohashi, Y. Kurita, T. Totani, H. Watanabe, T. Nakagawa, and M. Kubo, Bull. Chem. Soc. Japan, 35, 1317 (1962).
14. C. W. Heitsch, Inorg. Chem., 4, 1019 (1965).
15. A. J. Bannister and N. W. Greenwood, J. Chem. Soc., 1534 (1965)
16. G. E. Ryschkewitsch and W. J. Rademaker, J. Magnetic Res., 1, 584 (1969).
17. T. D. Coyle and F. G. A. Stone, J. Amer. Chem. Soc., 83, 4139 (1961).
18. J. S. Hartman and J. M. Miller, Inorg. Nucl. Chem Letters, 5, 831 (1969).
19. M. E. A. Davidson, J. S. Hartman, J. J. Klassen, and J. M. Miller, J. Chem. Soc. Dalton, 2603 (1972).
20. J. M. Miller and M. Onyszchuk, Canad. J. Chem. 44, 899 (1966).
21. M. J. Bula, D. E. Hamilton, and J. S. Hartman, J. Chem. Soc. Dalton, 1405 (1972); D.E. Hamilton, J. S. Hartman, and J. M. Miller, Chem. Comm., 1417 (1969).

22. R. E. Shuster, A. Fratiello, and T. Onak, J. Amer. Chem. Soc., 90, 1194 (1968); Chem. Comm., 1038 (1967)

23. E. Gore and S. S. Danylak, J. Phys. Chem., 69, 89 (1965).

24. D. E. McLaughlin, M. Tamres, and S. Searles, J. Amer. Chem. Soc., 82, 5621 (1960).

25. R. A. Craig and R. E. Richards, Trans. Faraday Soc., 59, 1962 (1963).

26. R. J. Gillespie and J. S. Hartman, Canad. J. Chem., 46, 2147 (1968).

27. S. J. Kuhn and J. S. McIntyre, ibid., 43, 375 (1965).

28. W. Gerrard, M. F. Lappert, and J. W. Wallis, J. Chem. Soc., 2141, (1960).

29. W. Gerrard, M. F. Lappert, H. Pyszora, and J. W. Wallis, ibid., 2144 (1960).

30. M. J. Bula and J. S. Hartman, ibid., (1973), in press.

31. M. Schmidt and H. D. Block, Chem. Ber., 103, 3705 (1970).

32. A. B. Burg and R. I. Wagner, J. Amer. Chem. Soc., 75, 3872 (1953).

33. Beilstein, "Handbuch der organischen Chemie," I, 16, 757.

34. Beilstein, ibid., I, 16, 758.

35. A. H. Cowley and J. L. Mills, J. Amer. Chem. Soc., 91, 2911 (1969).

36. G. M. Whitesides, J. L. Beauchamp, and J. D. Roberts, J. Amer. Chem. Soc., 85, 2665 (1963).

37. S. L. Manatt, G. L. Juvinall, R. I. Wagner, and D. D. Elleman, ibid., 88, 2690 (1966).

38. E. W. Abel, R. A. N. McLean, and I. H. Sabherwal, J. Chem. Soc. (A), 133 (1969).

39. A. H. Cowley and M. C. Damasco, J. Amer. Chem. Soc., 93, 6815 (1971).

40. G. Mavel, "Progress in Nuclear Magnetic Resonance Spectroscopy," Vol. I, J. W. Emsley, J. Feenery, and L. H. Sutcliffe, eds., Pergamon Press, Oxford, 1966, pp. 256 - 257.

41. J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance," Vol. I, Interscience Publishers, Inc., New York, 1958, p. 46.

42. J. S. Waugh and R. W. Fessenden, J. Amer. Chem. Soc., 79, 846 (1957).

43. G. Mavel, op. cit., p. 264.

44. H. S. Gutowsky, D. W. McCall, and C. P. Slichter, J. Chem. Phys., 21, 279 (1953).

45. N. Muller, ibid., 32, 359 (1962).

46. A. D. Walsh, Disc. Faraday Soc., 2, 18 (1947); H. A. Bent, Canad. J. Chem., 38, 1235 (1960).

47. G. R. Eaton and W. M. Lipscomb, "NMR Studies of Boron Hydrides and Related Compounds," W. A. Benjamin, New York, 1969, pp. 542 - 544.

48. D. F. Gaines, R. Schaeffer, and F. Tebbe, J. Phys. Chem., 67, 1937 (1963).

49. J. Davis and J. E. Drake, J. Chem. Soc. (A), 2959 (1970).

50. K. Hedberg and V. Schomaker, J. Amer. Chem.Soc., 73, 1482 (1951).

51. D. R. Martin and R. E. Dial, ibid., 72, 852 (1950); E. Wiberg and U. Heubaum, Z. anorg. allgem. Chemie, 225, 270 (1935).

52. C. A. Coulson, "Valence," 2nd Edition, Oxford University Press, London, 1961, pp. 204ff.

53. C. A. Barrus, J. Chem. Phys., 28, 427 (1958).

54. J. R. Durig, Y. S. Li, L. A. Carreira, and J. D. Odom, J. Amer. Chem. Soc., 95, 2491 (1973).

55. P. S. Bryan and R. L. Kuczkowski, Inorg. Chem., 11, 553 (1972).

56. E. Lee and C. K. Wu, Trans. Faraday Soc., 35, 1366 (1939).

57. J. A. Lannon and E. R. Nixon, Spectrochim. Acta, 23A, 2713 (1967).

CHAPTER III

HALOGEN REDISTRIBUTION REACTIONS IN PHOSPHINE BORON TRIHALIDE ADDUCTS

INTRODUCTION

Only quite recently have reports appeared in the literature pertaining to redistribution reactions among adducts of boron trihalides. Molecular addition compounds of mixed boron trihalides have been prepared with trimethylamine,[1-5] dimethyl ether,[6,7] dimethylsulfide,[8] and phosphines.[9] Phosphine haloboranes have also been recently reported.[10,11] Several of these reports have appeared while this work was in progress[3,4,5,7,8,9] and the publishing of portions of the work reported here may have contributed to the development of some of these investigations.[7,8]

Redistribution reactions among the free boron trihalides have, on the other hand, been long known and a fairly extensive literature pertaining to the mixed boron halide species has been reviewed in a number of surveys.[12-14] Only those aspects of this material which directly apply to the results of the present investigation will be briefly mentioned here.

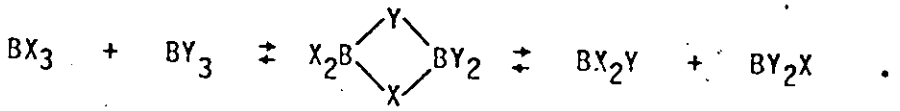
1. Halogen Redistribution among Free Boron Trihalides. With the exception of BBr_2I and $BBrI_2$,* the mixed boron trihalides have not been isolated and are observed to exist only in equilibrium with binary mixtures of the corresponding simple species. Although repeated efforts

---

*These were isolated by Besson in 1891.[15]

to produce the mixed species BF_2I and BFI_2[16,17] have not succeeded, the triple-mixed species BFClI and BFBrI have been observed by means of ^{11}B n.m.r. techniques.[17]

The redistribution of halogen atoms among boron trihalides is thought to proceed via the formation of bridge-bonded dimers,[18] not unlike the dimeric system, Al_2Cl_6:



The failure, however, to obtain conclusive experimental evidence for the existence of such dimers even at low temperatures leaves the mechanism of redistribution an open question.[19] Redistribution through an ionization route has also been proposed:[20]

$$BX_3 \;+\; BY_3 \;\rightleftarrows\; BX_2^+ \;+\; BY_3X^- \;\rightleftarrows\; BX_2Y \;+\; BY_2X \;.$$

Lappert and co-workers[21] have undertaken an ^{11}B n.m.r. investigation of the thermodynamics of halogen redistribution, the results of which have immediate bearing on the equilibrium study which follows. The equilibria resulting from the redistribution of two different substituents (as in the reaction $BX_3 + BY_3 \rightleftarrows BX_2Y + BXY_2$) may be described by a set of two independent expressions:

$$K_1 = \frac{[BX_2Y]}{[BX_3]^{2/3}\;[BY_3]^{1/3}}$$

and,

$$K_2 = \frac{[BXY_2]}{[BX_3]^{1/3}\;[BY_3]^{2/3}}$$

The relative concentrations of the various species were determined as mole percent by means of integrated peak area. The equilibrium constants for the various systems in methylcyclohexane and in 1,1-dichloroethane were determined along with free energies, standard enthalpy and entropy changes. The equilibrium constants differ slightly, but significantly, from what might be expected for a thermally neutral random distribution. (If one employs the equilibrium expression of Lappert and assumes a statistically random distribution for two exchanging substituents on one type of central moiety, namely, 1:3:3:1,[22] the ideal K_{eq} should be 3.) Only one system, the BBr_3/BCl_3 redistribution in 1,1-dichloroethane at 25°C, has a value slightly greater than 3. It appears then that the heats of redistribution of halogen atoms are nearly zero or slightly endothermic.[21,23] The data also suggest that the endothermicity increases with increasing electronegativity difference between the two halogens. This may help to explain the non-existence of BF_2I and BFI_2 in systems of free boron trihalides. Another interpretation of the deviation from randomness has been given in terms of the extent of boron-halogen π-bonding.[7]

2. Halogen Redistribution among Adducts of the Boron Trihalides.

Halogen redistribution among boron trihalide adducts is significantly affected by the nature of the donor molecule. It has been observed, for example, that in boron trihalide-trimethylamine systems, no halogen redistribution occurs in adduct mixtures.[1] For any given Me_3NBX_3 system redistribution does occur only in the presence of free excess Lewis acid. On the other hand, boron trihalide adducts of weaker Lewis bases such as

Me_2O,[6,7] and Me_2S,[8] do redistribute halogens even in the absence of free acceptor species. The necessity for excess boron acid to effect mixing in the trimethylamine series suggested a mechanism of redistribution involving a pre-ionization step:[3]

$$LBX_3 + BY_3 \rightleftarrows LBX_2^+ + BY_3X^- \rightleftarrows LBX_2Y + BY_2X \quad .$$

This mechanism was tested by means of a ^{10}B isotopic labelling experiment.[4] While confirming that the N-B bond remained intact during the halogen redistribution, an alternative to the first-order pre-ionization step was suggested. Conceivably, redistribution could occur via a halogen-bridged intermediate, in a second-order process. Gas phase N-B bond breaking with subsequent halogen mixing was observed when an equimolar mixture of $Me_3N^{10}BX_3$ and $Me_3N^{11}BY_3$ was heated to 160° C for 3 hours in a sealed, evacuated tube.[4] The behavior of the redistribution process in the weaker adducts does, however, leave open the possibility of a pre-dissociation step involving one or both adducts prior to halogen scrambling on boron.

The following account of halogen redistribution among the boron trihalide adducts is divided into two major parts:

1. The formation of the mixed boron trihalide adducts of phosphine and methyl-d_3-phosphine with emphasis on the ^1H n.m.r. parameters of the new adducts, the temperature dependence of the spectra, and the ordering of the mixed boron trihalide species in terms of relative Lewis acidity toward PH_3 and $MePH_2$. Redistribution reactions between the respective phosphine boranes and the boron trihalide adducts were also carried out and these results are reported as well.

2. The equilibrium study of halogen redistribution among the phosphine boron trihalide adducts. The results of this study are compared with those of Lappert referred to above.

In the preceding discussion care has been taken to avoid the use of the term "exchange" in referring to halogen redistribution. In the interest of clarity this term is reserved for the bond-making bond-breaking processes occurring at the P-B bonding site.

EXPERIMENTAL

1. The Formation of the Mixed Adducts PH_3BX_2Y and PH_3BXY_2 ($X \neq Y$ = F, Cl, Br). Equimolar quantities (ca. 0.5 mmole) of BX_3 and BY_3 were distilled into evacuated vessel D at -196°C together with phosphine (ca. 1.0 mmole). Essentially the same procedure was then followed as already described for the preparation of the simple PH_3BX_3 adducts.

2. The Formation of the Mixed Adducts PH_3BX_2I and PH_3BXI_2 (X = F, Cl, Br). The procedure employed followed that previously described for the preparation of PH_3BI_3 except for the on-line addition of BX_3 and of an estimated quantity of PH_3 to react with both acids.

3. The Formation of $PH_3BClBrI$. This adduct was prepared by mixing PH_3, BCl_3, BBr_3, and BI_3 in the approximate ratio 3:1:1:1.

4. The Formation of the Mixed Halogenoboranes, PH_3BXH_2 and PH_3BX_2H (X = Cl, Br, I). These adducts were prepared by reacting PH_3, B_2H_6, and BX_3 in the ratio 4:1:2.

5. <u>The Formation of the Adducts $CD_3PH_2BX_2Y$ ($X \neq Y = H, F, Cl, Br, I$)</u>. The mixed adducts of the boron trihalides with CD_3PH_2 were prepared in the same manner as that described for the PH_3 system (1 - 4). CH_2Cl_2 was used as solvent in these systems for the reasons given in the preceding chapter.

6. <u>The Equilibrium Study</u>. Reaction vessel C was employed in the equilibrium investigation. Each adduct was formed separately in different portions of the tube. Molar quantities of reactants were approximately double those of the typical preparations described above. After the formation of one adduct, mild warming was used to move it to the bottom of the reaction vessel. The second adduct was formed in the upper portion of the tube by collecting the appropriate BX_3 and PH_3 in this region at -196°C. Subsequent warming permitted adduct formation near this area. Methyl iodide was then distilled into the tube. (It was not necessary to use CD_3I since only the downfield PH resonance was studied. Hence there could be no interference from the methyl proton resonance.) When the system warmed to room temperature the adducts were mixed by gentle agitation. The system was kept at room temperature from 2 to 3 hours.

After equilibration the heterogeneous (solid-solution) phase was cooled to near -70°C and the solution was passed through the internal filter into the side-arm n.m.r. tube. The contents were frozen and the tube was sealed.

Spectra were recorded at -70°C and adduct concentrations were expressed in terms of ratios of integrated peak areas (mole percent).

RESULTS AND DISCUSSION

1. Halogen Redistribution. The ^1H n.m.r. parameters of all phosphine and methyl-d_3-phosphine adducts formed through halogen mixing are displayed in Table III - 1. All of the adducts were typified by low solubility although methyl substitution on phosphorus enhanced the solubility of the CD_3PH_2 adducts to some extent. Because it was found necessary to use different solvents for the two systems, as explained in the preceding chapter, parameters were obtained in selected cases in both solvents for comparison purposes (Table III - 1). The ^1H n.m.r. parameters of the unmixed systems are listed as obtained under two conditions: (1) those obtained as part of the single-species investigation, and (2) those observed as part of the present redistribution study. Although little discrepancy is to be noted between the sets of parameters for the tribromide and triiodide systems, some difference is apparent in the trichloride values, and a significant variance is seen in the case of CD_3-PH_2BF_3. (See APPENDIX, Section 3A for the complete listing of ^1H n.m.r. parameters in all eight mixed systems, of which Table III - 1 is a composite.) It may be that in the trifluoride system, donor-acceptor bond-making bond-breaking processes occur at very low temperatures. The possibility of exchange even at -70°C is perhaps suggested by the data for most of the systems as can be seen by consulting Section 3A of the Appendix. The ^1H n.m.r. parameters of adducts of unmixed BX_3 adducts do show some variation depending on the system of which they make a part. Interaction of free BX_3 with other adduct species present may possibly account for the variation in the recorded parameters.

TABLE III - 1

Observed ^1H n.m.r. parameters (δ in ppm ± 0.05 ppm relative to int. TMS; J_{PH} in Hz ±2 Hz) for the mixed boron trihalide adducts $(CD_3)_nPH_{3-n}BX_2Y$ and $(CD_3)_nPH_{3-n}BXY_2$ ($n = 0, 1$; $X \neq Y = Cl, Br, I$).

COMPOUND	Mixed		Single		COMPOUND	Mixed		Single	
	δ	J_{PH}	δ	J_{PH}		δ	J_{PH}	δ	J_{PH}
PH_3BI_3	-7.42	436	-7.48*	432*	$CD_3PH_2BI_3$	-6.22	434	-6.22	432
PH_3BBrI_2	-7.08	434			$CD_3PH_2BBrI_2$	-5.96	432		
PH_3BClI_2	-6.90	432			$CD_3PH_2BClI_2$	-5.88	430		
PH_3BBr_2I	-6.72	432			$CD_3PH_2BBr_2I$	-5.80	430		
$PH_3BClBrI$	-6.54	430							
PH_3BCl_2I	-6.42	430			$CD_3PH_2BCl_2I$	-5.62	426		
PH_3BBr_3	-6.44	428	-6.46*	430*	$CD_3PH_2BBr_3$	-5.62	430	-5.62	428
PH_3BClBr_2	-6.28	426			$CD_3PH_2BClBr_2$	-5.50	426		
PH_3BCl_2Br	-6.00	424			$CD_3PH_2BCl_2Br$	-5.40	426		
PH_3BCl_3	-5.90	420	-5.80	420	$CD_3PH_2BCl_3$	-5.37	428	-5.38†	426†
PH_3BFBr_2	~-6.0	~410			$CD_3PH_2BFBr_2$	-5.32	422		
					$CD_3PH_2BFCl_2$	-5.15	420		
PH_3BF_2Br	~-5.9	~404			$CD_3PH_2BF_2Br$	-5.02	406		
					$CD_3PH_2BF_2Cl$	-4.94	406		
					$CD_3PH_2BF_3$	-4.50	378	-4.26	355

*Recorded at -70°C in CH_2Cl_2.
†Recorded at -40°C in CD_3I.

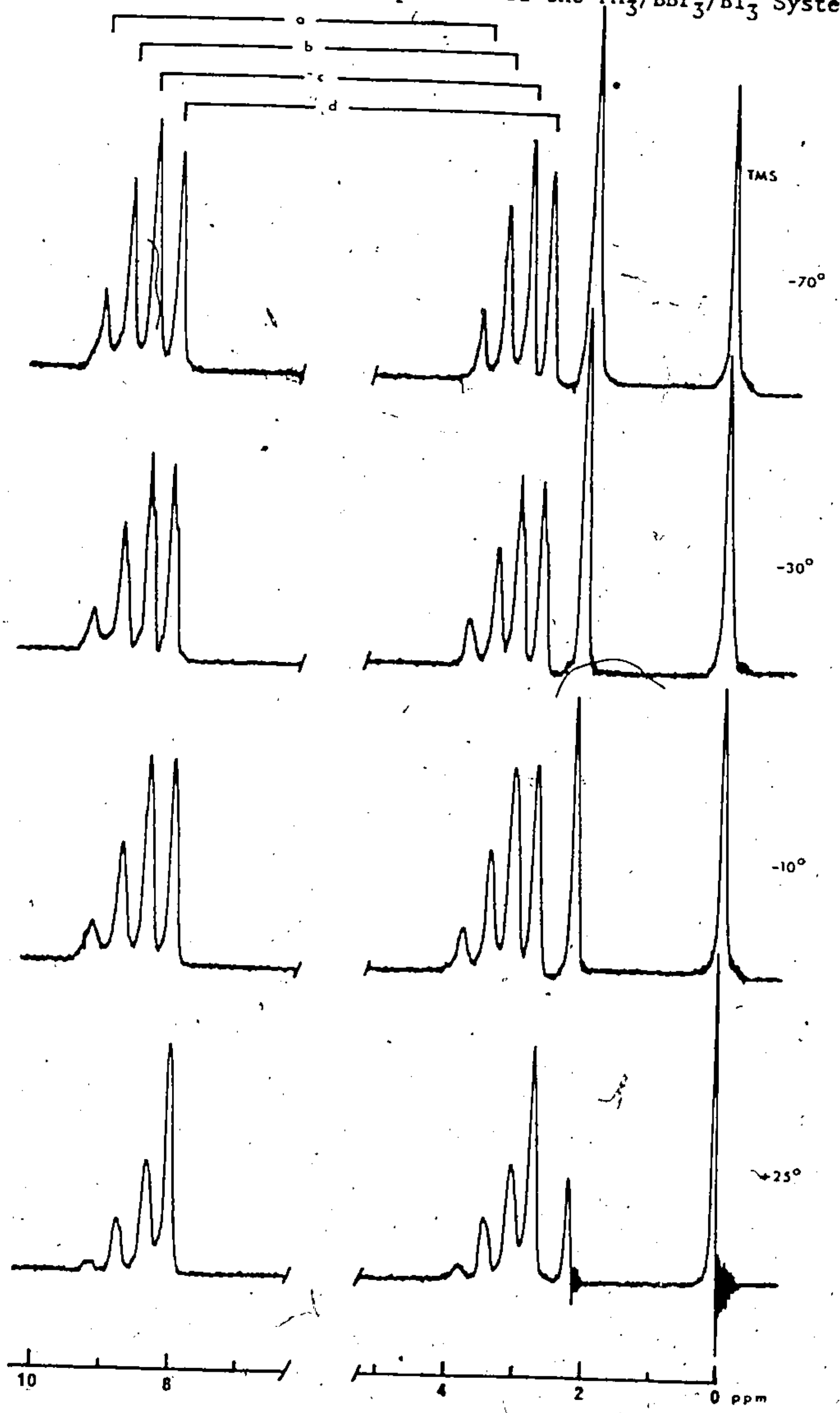
The $PH_3/BBr_3/BI_3$ System. When phosphine is mixed with approximately equimolar amounts of boron tribromide and boron triiodide the ^1H n.m.r. spectrum shows a series of four doublets attributable to the four adducts: (a) PH_3BI_3, (b) PH_3BBrI_2, (c) PH_3BBr_2I, and (d) PH_3BBr_3 (Table III - 1; Figure III - 1*). In view of the previously established parameters for PH_3BI_3 and PH_3BBr_3 in Chapter II, it seems reasonable to make the other assignments as indicated above, rather than to some extraneous component. Furthermore, as the results of the subsequent equilibrium study will show, the equilibrium constants for the redistribution remain relatively unchanged even when the initial ratios of PH_3BI_3 and PH_3BBr_3 are varied. Since K_{eq} values were computed on the assumption that the interpolated peaks were attributable to PH_3BBrI_2 and PH_3BBr_2I, the assignment seems to be reasonably sound.

The $PH_3/BCl_3/BI_3$ System. As discussed in the previous chapter the temperature dependence of ^1H n.m.r. spectra can be a qualitative indicator of relative degrees of adduct stability with respect to exchange processes between adduct and free base. Figure III - 2 provides a good example of this in terms of the single and mixed adducts of the $PH_3/BCl_3/BI_3$ system. At room temperature only the peaks attributable to PH_3BI_3 and PH_3BClI_2 can be clearly distinguished. There was little subsequent variation in the shape or position of these peaks as the system was cooled. Thus it may be concluded that for these two adducts at least, exchange

---

*Several of the spectra of BI_3 adducts exhibit a small shoulder on the proton resonance peak. The presence of this feature is difficult to explain. It may be that it arises from an impurity generated in situ by reaction between the PH_3BI_3 species and the solvent.

Figure III - 1 -- The ^{1}H n.m.r. Spectrum of the $PH_3/BBr_3/BI_3$ System



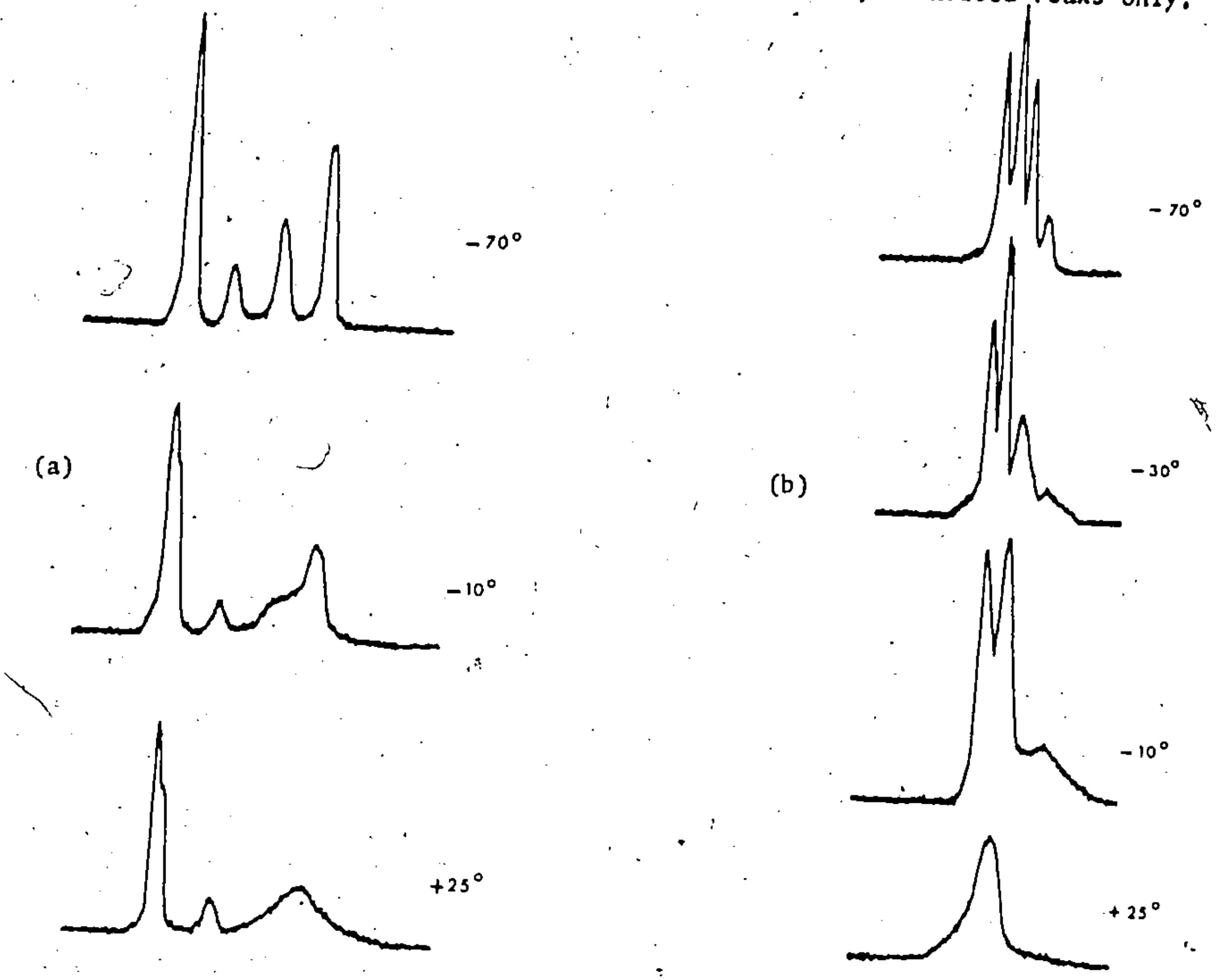


Figure III - 2 -- The ^{1}H n.m.r. Spectra of (a) the $PH_3/BCl_3/BI_3$ System and (b) the $PH_3/BCl_3/BBr_3$ System, recorded in CD_3I at various temperatures; Downfield Peaks only.

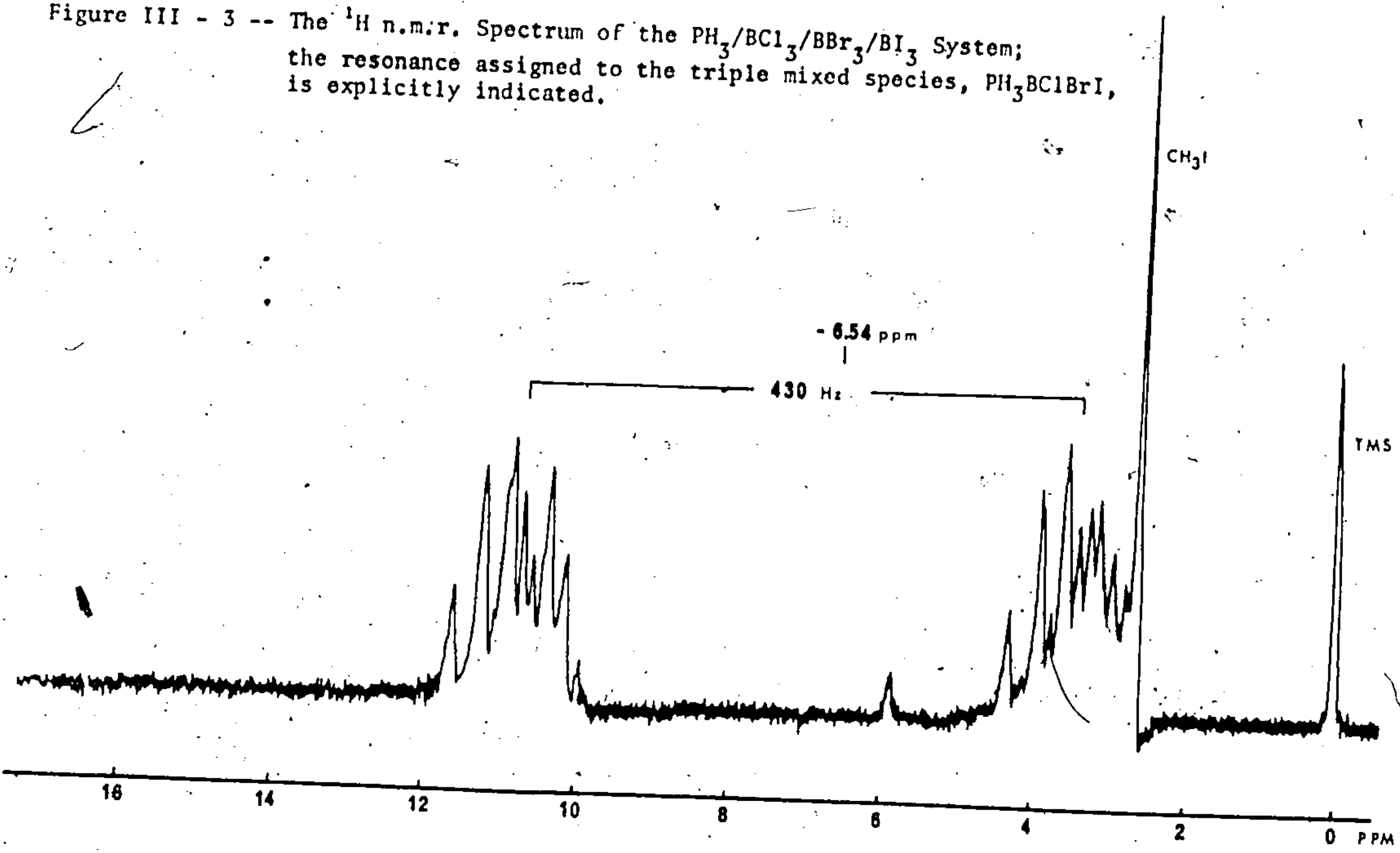
processes of the type $PH_3 + BX_3 \rightleftarrows PH_3BX_3$ are minimal. Only as the temperature of the system is lowered is the exchange process slowed sufficiently that the remaining two proton resonance peaks can be distinguished.

The $PH_3/BCl_3/BBr_3$ System. An examination of Figure III - 2(b) will indicate that in this system exchange is so rapid that the low field series of doublets appears as one envelope. As the system is cooled the individual peaks progressively appear: those attributable to PH_3BBr_3 and PH_3BClBr_2 at -10°C; PH_3BCl_2Br at -30°C; and PH_3BCl_3 at -70°C.

The $PH_3/BCl_3/BBr_3/BI_3$ System. Figure III - 3 exhibits nine sets of doublets, eight of which are assignable to mixed adduct species previously identified in terms of the ^1H n.m.r. parameters. The new resonance occurring at -6.54 p.p.m. relative to TMS with J_{PH} = 430 Hz has been assigned to the triple mixed species $PH_3BClBrI$.

Other Experiments and the CD_3PH_2 System of Adducts. The results of the previous investigation suggested that halogen redistribution might proceed via free boron trihalide. In anticipation of the equilibrium study and to test this idea further, an experiment was devised whereby PH_3BI_3 and PH_3BBr_3 were formed in separate portions of tube E and then mixed in solution at -70°C. The ^1H n.m.r. spectrum was then run immediately and gave no evidence for formation of the mixed adducts. The tube was warmed and the system held at room temperature for about 10 minutes. The spectrum run at -70°C now exhibited small resonance peaks attributable to the formation of the mixed species. After one hour at

Figure III - 3 -- The ^1H n.m.r. Spectrum of the $PH_3/BCl_3/BBr_3/BI_3$ System; the resonance assigned to the triple mixed species, $PH_3BClBrI$, is explicitly indicated.



room temperature the spectrum was virtually identical to that depicted in Figure III - 1.

When this same experiment was attempted with the $CD_3PH_2/BI_3/BBr_3$ system several hours elapsed before intermediate peaks of any significant magnitude were detected. After a few days at room temperature these exhibited considerable increase but there was also evidence of solvent interaction with free base.[24] The results of this experiment series supports the hypothesis that halogen redistribution proceeds via free boron trihalide, although other mechanisms can not be entirely ruled out. Much the same conclusion was reached on the basis of the experimental evidence associated with halogen redistribution in the Me_2O system.[7] The results also seem to indicate that methylphosphine is a stronger base than phosphine toward the boron halides, significantly reducing the amount of free boron acid because of the tighter donor-acceptor bond. Hence, the redistribution process among the BX_3 adducts of methylphosphine is a slower one.

In the free boron trihalide systems, the mixed BF_2Cl, $BFCl_2$, BF_2Br, and $BFBr_2$ species were observed but not BF_2I or BFI_2.[17] It was not surprising therefore that attempts to form the mixed adducts PH_3BF_2I and PH_3BFI_2 were unsuccessful. Attempts to prepare the mixed complexes PH_3BF_2Cl and PH_3BFCl_2 were likewise unsuccessful. This would seem to be predictable inasmuch as PH_3BF_3 itself does not form and consequently adduct formation between PH_3 and BF_2Cl and $BFCl_2$ may not be likely. However, peaks were discerned in the mixed $PH_3/BF_3/BBr_3$ system which suggests that the Lewis acidity of the acceptor is sufficiently enhanced by bromine substitution to allow the formation of PH_3BF_2Br and PH_3BFBr_2.

With this in mind it seemed appropriate to study a system in which a BF_3 adduct could be formed. Methylphosphine, apparently a stronger base than phosphine, was used as donor species. As can be seen from Table III - 1 the mixed adducts $CD_3PH_2BF_2Cl$ and $CD_3PH_2BFCl_2$ were obtained as well as the single species, $CD_3PH_2BF_3$. This lends additional support for the greater basicity of methylphosphine in these systems as contrasted with phosphine.

Finally, it is to be noted that although the complexes CD_3PH_2-BF_2I and $CD_3PH_2BFI_2$ were not observed in this system, the analogous adducts of trimethylamine have been reported.[1] This is especially noteworthy in that fluorine and iodine are incompatible in the free boron trihalide system. It also testifies to the exceptional strength of the donor-acceptor bond in the trimethylamine adducts and suggests that in this system halogen redistribution may indeed proceed by a radically different mechanism than it does in systems of weaker BX_3 adducts.

<u>The ^1H n.m.r. Parameters and Lewis Acidity</u>. The spectrum of the $PH_3/BBr_3/BI_3$ system (Figure III - 1) neatly illustrates the successive shifts to low field and the increase in coupling constant magnitude (Table III - 1) as the halogen changes from bromine through iodine. These trends are in fact remarkably consistent for all of the adducts. There is a similar set of trends in the more extensive series starting at $CD_3PH_2BF_3$ (δ = 4.50 p.p.m., J_{PH} = 378 Hz) through $CD_3PH_2BI_3$ (δ = 6.22 p.p.m., J_{PH} = 434 Hz). As observed in the preceding chapter, an

increase in the Lewis acidity of the boron halide results in a deshielding of the proton on phosphorus, so that the order of decreasing Lewis acidity, relative to these bases, is: $BI_3 > BBrI_2 > BClI_2 > BBr_2I > BClBrI > BCl_2I > BBr_3 > BClBr_2 > BCl_2Br > BCl_3 > BFBr_2 > BFCl_2 > BF_2Br > BF_2Cl > BF_3$. This corresponds to the order with respect to amines.[1,25] Although the change in J_{PH} from one adduct to the next is small, the trend toward larger values of the coupling constant with increasing acidity of the acceptor is apparent. The previously proposed relationship between increased s-character in the P-H bonding orbitals and increased acidity of the acceptor is maintained.

2. The Haloborane Adducts, $(CD_3)_nPH_{3-n}BHX_2$ and $(CD_3)_nPH_{3-n}BH_2X$ $(n = 0, 1; X = Cl, Br, I)$. A series of redistribution reactions between various BX_3 adducts and the corresponding phosphine or methyl-d_3-phosphine borane were carried out in a manner similar to that described for the halogen redistribution experiments. The ^1H n.m.r. parameters of the resulting adducts are given in Table III - 2. The spectrum of the $PH_3/B_2H_6/BBr_3$ system is displayed in Figure III - 4.

The chemical shifts of the PH_3 series decrease in the order: $BHI_2 > BHBr_2 > BH_2I > BHCl_2 > BH_2Br > BH_2Cl > [BH_3]$. In the methylphosphine series, the adducts of BH_2I and $BHBr_2$ are observed to interchange order. For both series, however, a regular progression in coupling constant values is observed: $BHX_2 > BH_2X > [BH_3]$; and within any specific X-series the order decreases from I through Cl. The general trend to be noted in both chemical shift and coupling constant parameters is parallel to that observed in the foregoing investigation and in Chapter II, namely,

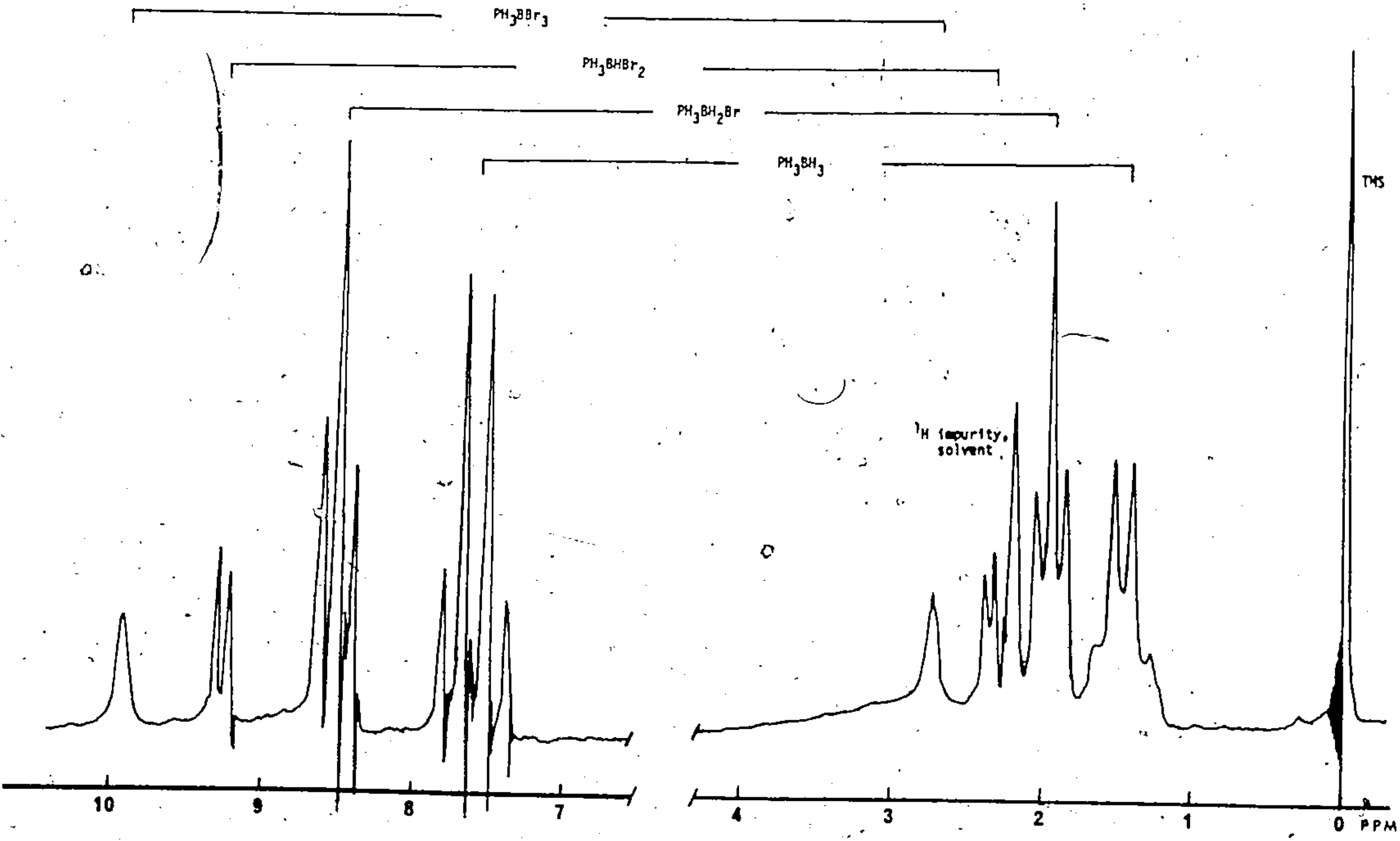
TABLE III - 2

Observed ^1H n.m.r. parameters (δ in ppm ± 0.05 ppm relative to int.TMS; J_{PH} in Hz ± 2 Hz) for the mixed haloborane adducts $(CD_3)_nPH_{3-n}BH_2X$ and $(CD_3)_nPH_{3-n}BHX_2$ ($n = 0, 1$; $X = Cl, Br, I$) in CD_3I at - 70°C.

COMPOUND	δ	J_{PH}	$J_{HH'}$	COMPOUND	δ	J_{PH}	$J_{HH'}$
$PH_3BH'I_2$	-6.50	422	4.5	$CD_3PH_2BH'I_2$	-5.81	420	-
$PH_3BH'Br_2$[a]	-5.88	418	4.5	$CD_3PH_2BH'Br_2$	-5.26	416	-
$PH_3BH'Cl_2$[a]	-5.39	415	4.5	$CD_3PH_2BH'Cl_2$	-5.10	406	-
$PH_3BH_2'I$	-5.62	400	6.0	$CD_3PH_2BH_2'I$	-5.44	405	6.0
$PH_3BH_2'Br$[a]	-5.30	396	6.0	$CD_3PH_2BH_2'Br$	-5.01	395	6.0
$PH_3BH_2'Cl$[a]	-5.01	394	6.0	$CD_3PH_2BH_2'Cl$	-4.90	389	6.0
PH_3BH_3'[a]	-4.60	368	8.5	$CD_3PH_2BH_3'$[b]	-4.61	377	8.0

a) See ref. 11 for slightly different values obtained under other conditions.
b) See ref. 26 for slightly different values obtained under other conditions.

Figure III - 4 -- The ^1H n.m.r. Spectrum of the $PH_3/B_2H_6/BBr_3$ System recorded in CD_3I at -70°C.



that as the acceptor species increases in acidity more s-character concentrates in the P-H bonding orbitals and a greater deshielding of protons on the donor occurs. The magnitude of the indirect coupling constant, $J_{HH'}$, decreases as the number of hydrogens on boron decreases. The nature of the halogen substituent does not seem to have any noticeable effect on this parameter, but the over-all change is so small that it is difficult to say for sure. Although $J_{HH'}$ was resolvable for the phosphine adducts of BHX_2 this was not the case for the analogous methylphosphine compounds.

Attempts to prepare mixed-BHF_2 and BH_2F adducts with CD_3PH_2 produced ambiguous results. The ^1H n.m.r. spectrum consisted of a set of coalescing peaks which remained unresolved even at very low temperatures (-90°C in CH_2Cl_2) and large scale expansions.

It is worthy of note that when CD_3PH_2 adducts were formed in separate portions of the reaction tube and subsequently intermingled in the presence of solvent, mixed adducts were observed for the $[BH_3]/BCl_3$ and $[BH_3]/BBr_3$ systems but not for the $[BH_3]/BI_3$ system. Only after several days at room temperature were any intermediate peaks discernable in the latter case. Direct boron-hydrogen coupling, $J_{BH'}$, was not observed in the spectra of any of the adducts.

To assume that the phosphine haloboranes form by way of the same redistribution mechanism(s) as do the mixed adducts of the BX_3/BY_3 series may be somewhat risky. For this reason the system has been treated separately in this account. Furthermore, the series is not included in the following equilibrium study because a preliminary investigation gave no consistent values for the equilibrium "constants" of the redistribution process. In addition, only for redistribution reactions involving simple boron trihalides were comparable data available for reference purposes.

3. The Equilibrium Study of Halogen Redistribution. The equilibrium constants for the redistribution of two different substituents on the same central moiety of each adduct are given, after the manner of Lappert et al., in terms of the two independent expressions:[21]

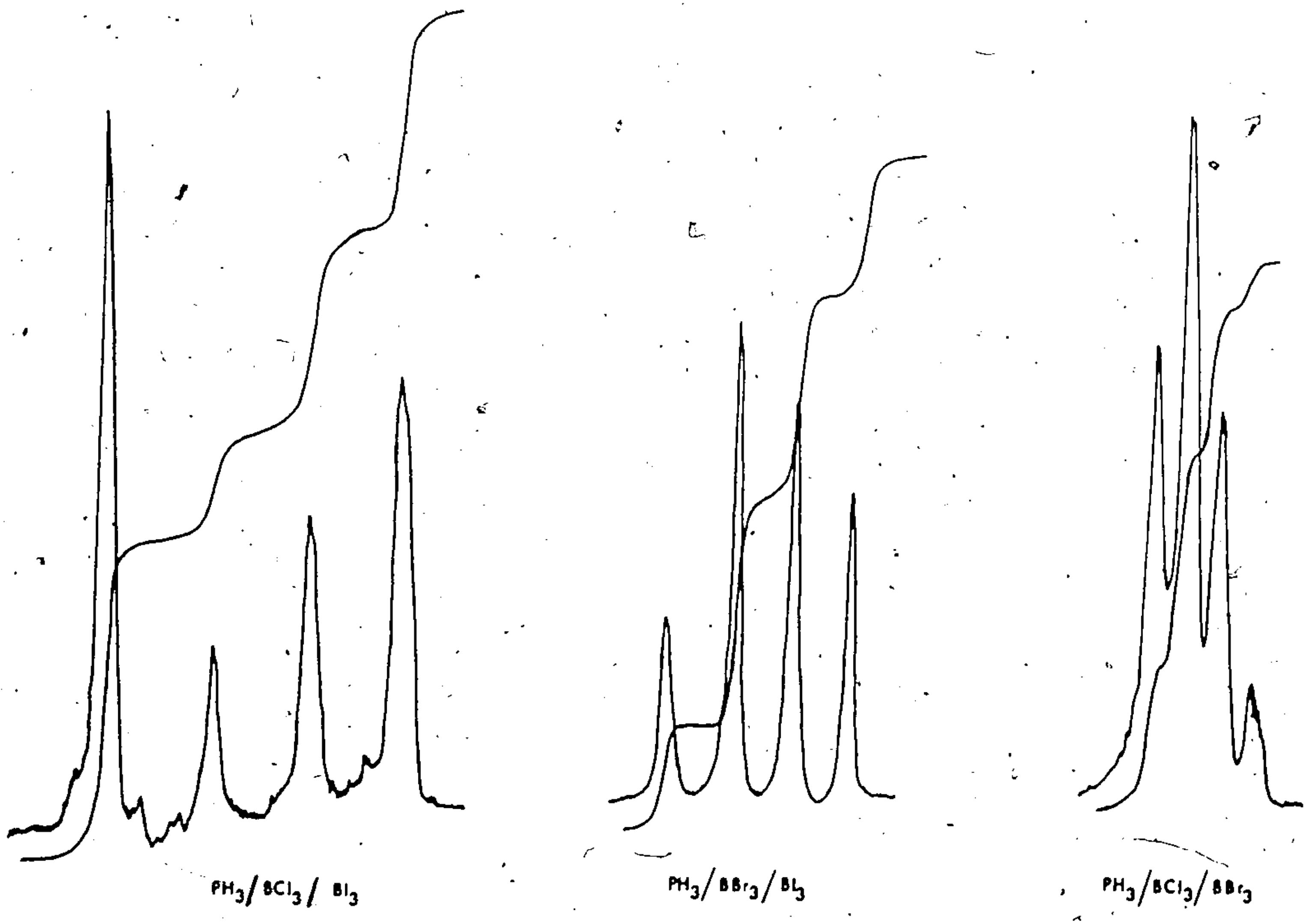
$$K_1 = \frac{[PH_3BX_2Y]}{[PH_3BX_3]^{2/3} [PH_3BY_3]^{1/3}}$$

and,

$$K_2 = \frac{[PH_3BXY_2]}{[PH_3BX_3]^{1/3} [PH_3BY_3]^{2/3}}$$

In each of the three series PH_3BCl_3/PH_3BI_3, PH_3BBr_3/PH_3BI_3, and PH_3BCl_3/PH_3BBr_3, eleven different ratios of starting amounts of adduct were used. After equilibration the n.m.r. spectrum of the low field peaks was recorded and the peak areas were integrated. The equilibrium constants K_1 and K_2 were calculated assuming that the mole percent of each component in the mixture was proportional to the area under each respective peak. An example of the low field integrated spectrum from each of the three series is given in Figure III - 5. The data for all of the runs are presented in Section 3B of the Appendix, Tables 3B - 1 through 3B - 3. In a few cases, the extent of equilibration was tested by repeating the spectrum after one day. The relative consistency between spectra gave reasonable assurance that the systems were at equilibrium

Figure III - 5 -- Integrated Peak Areas of the Downfield Resonance for each Redistribution System.



when initially studied.

A summarization of the data is given below in Table III - 3. Average K_1 and K_2 values are given for each system and compared with the corresponding values from the free boron trihalide system. The errors quoted are equal to twice the standard deviation of the mean, $\sigma = 2\left(\frac{\Sigma x - \bar{x}}{n}\right)^{\frac{1}{2}}$., paralleling the free boron trihalide investigation. The low concentrations of the various components reduced the accuracy of the integration and may be a reason for the larger margin of error. Nevertheless, in all instances the equilibrium values for the adduct redistribution reactions are not very different from those obtained in the original study. The PH_3BCl_3/PH_3BBr_3 system exhibits the greatest extent of departure while the values of the PH_3BBr_3/PH_3BI_3 system are very close to those of the "free" system.

The thermodynamic parameters of the the boron trihalide redistribution indicate that the reactions are close to thermal neutrality or slightly endothermic. The similarity of equilibrium constants for the corresponding adduct systems suggests that this condition obtains in their case as well. A study of the variation of K_1 and K_2 with temperature would have afforded the opportunity to make quantitative assessments of the enthalpies of redistribution, but the coalescence of peaks at lower temperatures prevented this procedure. Instead, a somewhat speculative evaluation, based on the similarities between the two systems must suffice.

Hartman *et al.*,[7] have carried out a similar study on the dimethyl ether adducts of the boron trihalides. Using the equilibrium expressions:

TABLE III - 3

Equilibrium constants for halogen redistributions (1) and (2) for the phosphine boron trihalide adducts and the free boron trihalides with thermodynamic parameters for the later system

	BCl_3/BI_3	BBr_3/BI_3	BCl_3/BBr_3
K_1 adduct	0.47 ± 0.19	1.85 ± 0.28	2.49 ± 0.41
K_2 adduct	0.18 ± 0.11	1.94 ± 0.34	2.71 ± 0.55
K_1 free	0.94 ± 0.07	1.99 ± 0.08	3.84 ± 0.11
K_2 free	0.80 ± 0.03	1.73 ± 0.12	3.32 ± 0.11
ΔG^o_1 free	+0.04 $\frac{\text{kcal}}{\text{mole}}$	-0.42 $\frac{\text{kcal}}{\text{mole}}$	-0.82 $\frac{\text{kcal}}{\text{mole}}$
ΔG^o_2 free	+0.14	-0.33	-0.73
ΔH^o_1 free			+0.30
ΔH^o_2 free			+0.35
ΔS^o_1 free			+2.64 $\frac{\text{cal}}{\text{mole-deg}}$
ΔS^o_2 free			+2.92

$$K_1 = \frac{[Me_2OBX_2Y]\ [Me_2OBY_3]}{[Me_2OBXY_2]^2}$$

and

$$K_2 = \frac{[Me_2OBX_3]\ [Me_2OBXY_2]}{[Me_2OBX_2Y]^2}$$

it was found that the redistribution of halogens is much closer to the ideal random case (K = 0.33) in the Me_2O adducts than in the free trihalides. It is conjectured that this may result because tetrahedral

BX_3 will be unhampered by the π-back-bonding present in the planar species. Since the equilibrium data of the phosphine adduct system are similar to those of the free system, one might speculate that an important mechanism of redistribution among the phosphine adducts involves interaction between pairs of free boron trihalides.

REFERENCES

1. J. S. Hartman and J. M. Miller, Inorg. Nucl. Chem. Letters, 5, 831 (1969).

2. G. E. Ryschkewitsch and W. J. Rademaker, J. Magnetic Res., 1, 584 (1969).

3. S. S. Krisnamurthy and M. F. Lappert, Inorg. Nucl. Chem. Letters, 7, 919 (1971).

4. B. Benton-Jones and J. M. Miller, ibid., 8, 495 (1972).

5. B. Benton-Jones, M. E. A. Davidson, J. S. Hartman, J. J. Klassen, and J. M. Miller, J. Chem. Soc. Dalton, 2603 (1972).

6. D. E. Hamilton, J. S. Hartman, and J. M. Miller, Chem. Comm., 1417 (1969).

7. M. J. Bula, D. E. Hamilton, and J. S. Hartman, J. Chem. Soc. Dalton, 1405 (1972).

8. M. J. Bula and J. S. Hartman, Abstracts of the 55th Canadian Chemical Conference, Quebec City, June 5 - 7, p. 77.

9. G. Jugie, J. P. Laussac, and J. P. Laurent, Compt. Rend. Sc. Paris, 269C, 689 (1969).

10. J. P. Laussac, G. Jugie, and J. P. Laurent, Bull. Soc. chim. Fr., 2542, 4238 (1970).

11. J. E. Drake and J. Simpson, J. Chem. Soc. (A), 974 (1968).

12. M. F. Lappert, Chem. Revs., 56, 959 (1956).

13. J. C. Lockhart, ibid., 65, 131 (1965).

14. A. G. Massey, Adv. Inorg. Chem. Radiochem., 10, 1 (1967).

15. A. Besson, Compt. Rend., 112, 1001 (1891).

16. P. N. Gates, E. F. Mooney, and D. C. Smith, J. Chem. Soc., 3511 (1964).

17. M. F. Lappert, M. R. Litzow, J. B. Pedley, and A. Tweedale, J. Chem. Soc. (A), 2426 (1971).

18. F. E. Brinkman and F. G. A. Stone, J. Amer. Chem. Soc, 82, 6235 (1960) and references therein.

19. R. E. Steinhardt, G. E. Fetsch, and M. W. Jordan, J. Chem. Phys., 43, 4528 (1965).

20. L. H. Long and D. Dollimore, J. Chem. Soc., 4457 (1954).

21. M. F. Lappert, M. R. Litzow, J. B. Pedley, T. R. Spalding, and H. Nöth, J. Chem. Soc. (A), 383 (1971).

22. K. Moedritzer, Adv. Organometallic Chem., 6, 171 (1968).

23. A. Finch and P. J. Gardner, Prog. Boron Chem., 3, 177 (1970).

24. T. D. Coyle and F. G. A. Stone, J. Amer. Chem. Soc., 83, 4138 (1961).

25. J. M. Miller and M. Onyszchuk, Canad. J. Chem., 42, 1518 (1964).

26. J. Davis and J. E. Drake, J. Chem. Soc. (A), 2094 (1971).

CHAPTER IV

THE ^{11}B NUCLEAR MAGNETIC RESONANCE INVESTIGATION

INTRODUCTION

^{11}B chemical shifts have been considered to reflect the electron density or shielding at the boron nucleus.[1,2] In accord with this is the observation that when triply bonded boron forms 1:1 adducts with Lewis bases an upfield shift in the ^{11}B resonance occurs (See $\Delta\delta_{^{11}B}$ values, Tables IV - 1, -2, -3). The increased shielding of the boron nucleus upon adduct formation is consistent with an increase in electron density at boron provided by the donor species. It would seem to be a reasonable expectation that the order of ^{11}B chemical shifts for a series of 1:1 molecular addition compounds of fixed boron acceptor may be a useful indicator of relative donor strength toward that acceptor species. A variety of donor-BX_3 investigations have been undertaken in which donor strengths were evaluated on this basis. Both $\delta_{^{11}B}$ and $\Delta\delta_{^{11}B}$ ($\delta_{^{11}B}$adduct - $\delta_{^{11}B}BX_3$) were employed as indicators of relative basicities of pyridine, triethylamine and benzophenone toward the boron trihalides.[3] While verifying that the order of acid strength was constant regardless of the donor used and in accord with expectation: $BI_3 > BBr_3 > BCl_3 > BF_3$, orders of donor strength varied as a function of the acid. In the BF_3 system, ^{11}B resonance shifts indicated a decrease in shielding, and hence in donor strength as $Py > Et_3N > Ph_2CO$. In contrast, toward BBr_3 the order was $Ph_2CO > Py > Et_3N$. Assuming no difference in hybridization of the donor species in corresponding adducts, the variation in orders of donor strength was attributed to the extent of face-to-face steric hindrance (F-strain)[4] encountered between donor and acceptor. In a parallel study of ethyl acetate and some of its RCO_2Et_2 derivatives,[5] ^{11}B chemical shifts were again observed to vary as a function of the acceptor species. The "F-strain" hypothesis was further tested with a series of boron trihalide adducts of alkyl-substituted pyridines.[6] In this case the orders of basicity were observed to be the same toward each acid. More surprising, however, was that the order of relative basicity as interpreted from ^{11}B resonance shifts was found to be: 2-ethylpyridine > 4-ethylpyridine, which is just opposite to expectation on the basis of F-strain predictions.

Clearly, ^{11}B chemical shifts are not sensitive indicators of donor strength. Additional evidence for this is to be seen in the experimental results of the investigation which follows (Table IV - 7). In a theoretical treatment of chemical shifts,[7] nuclear shielding was discussed as the sum of three contributions: $\sigma = \sigma_d + \sigma_p + \sigma_o$. The diamagnetic term, σ_d, depends upon the electron distribution in the ground state of the molecule. The paramagnetic term, σ_p, derives from the mixing of ground and low-lying excited states under the influence of the imposed magnetic field. This term can have a dominant influence on shift if there is an asymmetric distribution of p-electrons around the nucleus.* The term σ_o is the contribution from other atoms or groups in the molecule. In a theoretical calculation of ^{11}B chemical shifts in the boron trihalides,[9] the paramagnetic term has been shown to be of dominant influence.

---

*Considerations similar to this have also been used in discussing ^{31}P chemical shifts.[8]

Although a simple relationship between donor strength and ^{11}B shift data is not to be expected, it is still useful (in view of the following account) to tabulate the ^{11}B chemical shifts for a number of adducts of simple donors with boron acids.

1. Nitrogen and Phosphorus Donors. The chemical shift of $[BH_3]$ has been computed as -57 p.p.m. relative to boron trifluoride etherate, Et_2O-BF_3.[10] An examination of the $\Delta\delta_{^{11}B}$ values ($\delta_{^{11}B}$ adduct - $\delta_{^{11}B}$ $[BH_3]$) for the adduct series $Me_nNH_{3-n}BH_3$ (Table IV - 1) will reveal a large upfield trend upon adduct formation. Nevertheless, it is to be noted that the actual ^{11}B resonance shifts follow an order opposite to the generally accepted trend of donor basicity (see Chapter 1, p. 14). It may be noted in passing that J_{BH} values vary from 91 to 98 Hz and do follow the established order of gas-phase basicity.

Trimethylamine[12] and trimethylphosphine[11,13] have been employed as reference bases in adduct formation with BX_3 acids. It should be noted that in Table IV - 2, except for the $[BH_3]$ adducts, the $\Delta\delta_{^{11}B}$ values follow the order of Lewis acidity.

Without attempting to minimize the danger of interpreting chemical shift values on a simple basis or in terms of any one single factor, it is intriguing to compare corresponding congener adduct values. When $\delta_{^{11}B}$ of a nitrogen adduct is compared to that of the corresponding phosphorus adduct, the shift is to higher field for the latter, implying that there is a greater drift of charge toward boron. When BF_3 is used as a reference acid, relative positions of chemical shift are reversed, suggesting a lessened transfer of charge by the phosphine donor as

TABLE IV - 1

The ^{11}B chemical shifts[11] in p.p.m. relative to ext Et_2OBF_3 for the $[BH_3]$ adducts of Me_nNH_{3-n}.

	δ_{11B}	$\Delta\delta_{11B}$
H_3NBH_3	+23.8	81
MeH_2NBH_3	+20.5	78
Me_2HNBH_3	+14.2	71
Me_3NBH_3	+ 8.1	65

TABLE IV - 2

The ^{11}B chemical shifts[11-13] in p.p.m. relative to ext Et_2OBF_3 for the BX_3 adducts (X = H, F, Cl, Br, I) of Me_3N and Me_3P.

	δ_{11B}	$\Delta\delta_{11B}$
Me_3NBH_3	+ 8.1	65
Me_3NBF_3	+ 0.3	11
Me_3NBCl_3	-10.2	36
Me_3NBBr_3	+ 3.1	42
Me_3NBI_3	+54.1	47
Me_3PBH_3	+39.1	96
Me_3PBF_3	- 0.1	10
Me_3PBCl_3	- 2.1	44
Me_3PBBr_3	+15.4	54

compared to the amine donor.[13]

2. <u>Oxygen and Sulfur Donors</u>. The ^{11}B chemical shift values for the analogous dimethylether[14] and dimethylsulfide[15] adducts with boron trihalides are displayed in Table IV - 3. It is evident that the same type of behavior noted above for the Group V donors also obtains for these two series of Group VI bases.

TABLE IV - 3

The ^{11}B chemical shifts[14,15] in p.p.m. relative to ext Et_2OBF_3 for the BX_3 adducts (X = H, F, Cl, Br, I) of Me_2O and Me_2S.

	$\delta_{^{11}B}$	$\Delta\delta_{^{11}B}$
Me_2OBH_3[13]	- 1.6	59
Me_2OBF_3	+ 0.7	12
Me_2OBCl_3	-10.7	36
Me_2OBBr_3	+ 4.2	43
Me_2SBH_3[13]	+21.0	69
Me_2SBF_3	- 2.2	8
Me_2SBCl_3	- 6.2	41
Me_2SBBr_3	+12.1	51
Me_2SBI_3	+69.6	65

The utility of $\delta_{^{11}B}$ or $\Delta\delta_{^{11}B}$ as an indicator of adduct stability has not received notable attention in previous investigations. But in the discussion of the results of this investigation some attention will be given to this topic.

As alluded to in an earlier chapter, the large nuclear quadrupole moment of the boron nucleus can be a source of difficulty in the determination of coupling constants when the spectrum of a nucleus attached to boron is recorded. On the other hand, neither ^1H nor ^{31}P nuclei possess nuclear quadrupole moments. As a result the ^{11}B spectra of compounds in which both or either nucleus is attached to boron afford the clearest and most precise determination of J_{PB} and J_{BH}.

The magnitude of the phosphorus-boron coupling constant, J_{PB}, has been examined as to its utility as a predictive indicator of Lewis acidity and basicity. The number of investigations has necessarily been limited by the requirement of a phosphorus donor, but two recent studies have yielded some interesting results. In one investigation[16] an empirical correlation was established between the magnitude of J_{PB} and the strength of the dative bond in the $[BH_3]$ adducts of a series of smoothly varying phosphine ligands such as F_nPH_{3-n}, Me_nPH_{3-n}, $(Me_2N)_nPF_{3-n}$, and F_2XP (X = F, Cl, Br). The general applicability of the study is, however, limited by the use of a single reference acid, $[BH_3]$.

In the second investigation[17] the magnitude of J_{PB} is correlated with the base strength of some 15 phosphine ligands. The data for two series of phosphines was obtained from the previous literature.[18-20] Base displacement reactions were used in selected cases to test the validity of the J_{PB} correlation. Again, the study was limited by the use of only one acceptor species, namely, $[BH_3]$.

The use of borane as the acceptor species did, however, permit the determination of a series of boron-hydrogen coupling constants. The magnitude of J_{BH} for a series of phosphine adducts was observed to increase in a manner roughly parallel to the increasing "π-acceptor ability" of the donors as previously determined on the basis of CO stretching frequencies. The values of J_{BH} ranged from 97.4 to 107 Hz. It was pointed out that the apparent correlation of these two parameters may possibly be only accidental and more data would be necessary before any diagnostic value could be attached to the magnitude of J_{BH}.

EXPERIMENTAL

1. The Formation of the Single Adducts $R_nPH_{3-n}BX_3$ (R = Me, Ph; n = 0, 1, 2; X = H, F, Cl, Br, I). All procedures were carried out as described previously in Chapter II. A small capillary containing external standard Et_2OBF_3 was inserted into the reaction vessels prior to use.

2. The Formation of the Mixed Adducts $Me_nPH_{3-n}BX_2Y$ and $Me_nPH_{3-n}BXY_2$ (n = 0, 1; X ≠ Y = Cl, Br, I). The mixed adducts were prepared by the addition of the requisite donor to a pre-equilibrated mixture of two simple boron trihalides, following the procedures outlined in Chapter III.

3. The Formation of the Separate Adducts PH_3BH_2X (X = Br, I). Equal quantities (ca. 4 mmole) of PH_3 and B_2H_5X were distilled into reaction vessel C at -196°C. Reactants were maintained at -23°C for four hours. Diborane was formed according to the equation:

$$PH_3 + B_2H_5X \rightarrow PH_3BH_2X + \tfrac{1}{2} B_2H_6 ,$$

and was monitored at -78°C before being pumped away. The adducts formed were rather viscous liquids. Solvent was added, the contents were

were internally transferred to the side-arm n.m.r. tube containing a Et_2OBF_3 reference capillary. The contents were frozen and the tube was sealed.

4. The Formation of the Separate Adducts PH_3BHX_2 (X = Br, I). The same procedure was followed as outlined above for the preparation of the PH_3-BH_2X adducts. After a nearly stoichiometric quantity of diborane had been monitored and pumped away, an appropriate quantity of HX was distilled into the vessel at -196°C. The reactants were maintained at -23°C for 12 hours. Hydrogen was formed according to the equation:

$$PH_3BH_2X \quad + \quad HX \quad \rightarrow \quad PH_3BHX_2 \quad + \quad H_2 \ ,$$

and was monitored periodically during the course of the reaction before being pumped away at -196°C. The adducts were white solids, relatively soluble in CH_3I. When the reaction had reached completion, the same procedures were followed as outlined above.

5. The Formation of the Separate Adducts PH_3BH_2Cl and PH_3BHCl_2. The instability of B_2H_5Cl[21] as a starting material required that some other means be used to prepare the monochloro- and dichloroborane adducts. In a typical experiment, ca. 4 mmole of PH_3BH_3 was formed in reaction vessel C in the usual fashion. An equal quantity of HCl was then admitted to the tube if the monochlorinated species was desired. Twice that amount was taken to prepare the dichloroborane adduct. The reactants were maintained at -23°C for 3 to 4 hours. Reaction progress was monitored in terms of the quantity of hydrogen produced. Disproportionation was not avoided entirely, but this method did yield adducts sufficiently pure for valid spectral analysis.

RESULTS AND DISCUSSION

1. The ^{11}B Chemical Shifts. The chemical shift values for all of the unmixed BX_3 adducts as well as for the free boron acids[22] are given in Table IV - 4. As expected, the increased shielding of the boron atom upon adduct formation is reflected in the upfield trend of the coupling constants of the adducts relative to those of the free BX_3 species. Within any given boron halide series this change is relatively constant and, interpreting this in terms of the σ-bonding model,[18,19] it supports the assumption that the boron acceptor does indeed present a nearly constant positive field to the various Lewis bases. The various mean shift differences, $\bar{\Delta}\delta_{^{11}B} = \frac{\Sigma\ \delta_{^{11}B}\text{ adduct} - \delta_{^{11}B}\ BX_3}{n}$, for each boron trihalide series are displayed in Table IV - 5. A comparison of these values with those found in Table IV - 2 and IV - 3 reveals that $\Delta\delta_{^{11}B}$ is only sensitive to gross changes in the donor species. (The differences in $\Delta\delta_{^{11}B}$ are generally more pronounced between Second and Third Row congeners than between donors having Group V and Group VI atoms of the same row.) These results highlight the observation that the ^{11}B chemical shift is not a sensitive indicator of donor strength.

It should be noted from the table that the mean chemical shift difference does increase in a manner parallel to the accepted order of Lewis acidity: $BI_3 > BBr_3 > BCl_3 > BF_3$. As observed in a previous study,[23] the chemical shift difference between the adducts and the planar compounds exhibits a qualitatively inverse relation to the extent of back-coordination in the planar species.

TABLE IV - 4

The observed ^{11}B n.m.r. parameters (δ in p.p.m. ± 1 p.p.m. relative to ext Et_2OBF_3;† J_{PB} in Hz ± 5 Hz) for the adduct series $R_nPH_{3-n}BX_3$ (R = H, Me, Ph; n = 0, 1, 2; X = H, F, Cl, Br, I) recorded at -30°C.

	$[BH_3]$			BF_3		BCl_3		BBr_3		BI_3	
	δ	J_{PB}	J_{BH}	δ	J_{PB}	δ	J_{PB}	δ	J_{PB}	δ	J_{PB}
a	-57.0^b			-10.8		-46.6		-39.1		+ 5.9	
PH_3	+43.0 (+43.4)	24 (27)	103 $(104)^c$	-	-	- 1.7	-	+21.5	132	+90.8	122
$MePH_2$	+41.0 (+41.5)	38 (43)	101 $(100)^d$	- 2.0	-	- 1.5	151	+19.0	149	+80.0	130
Me_2PH	+38.0 (+38.8)	55 (58)	98 $(96)^{d,e}$	- 1.5	43^h	- 3.0	163	+16.0	156	+73.0	134
$Me_3P^{f,g}$	(+39.0)	(62)	(95)	(- 0.1)	(174)	(- 2.0)	(166)	(+15.5)	(165)	-	-
$PhPH_2$	+42.0 (+41.4)	34 (35)	103 $(101)^d$	- 3.5	-	- 3.5	142	+17.0	139	+77.0	120
Ph_2PH	+39.5	36	101	- 4.5	-	- 2.5	161	+18.5	144	+78.5	127

† Literature values are adjusted to the external reference Et_2OBF_3: $\delta_{Et_2OBF_3} = \delta_{B(OCH_3)_3} - 17.4$ ppm.

a) Ref. 22 ; chemical shift values of the free boron acids.
b) Ref. 10
c) Ref. 18
d) Ref. 17
e) Ref. 2
f) Ref. 11
g) Ref. 13
h) J_{BF} = 55 Hz

TABLE IV - 5

The ^{11}B mean shift differences in p.p.m. of each boron trihalide adduct with the donor series R_nPH_{3-n} (R = Me, Ph; n = 0, 1, 2).

Boron Trihalide	$\bar{\Delta}\delta_{^{11}B}$
BF_3	+ 8
BCl_3	+44
BBr_3	+57
BI_3	+74

The stabilities of the various adducts with respect to dissociation, as estimated on the basis of the ^1H n.m.r. temperature dependent study (Table II - 4; APPENDIX, Tables 2A - 1 through 2A - 5), also parallels this order. It is however in this respect that the atypical behavior of $[BH_3]$ toward Lewis bases is apparent. The average $\Delta\delta$, computed on the basis of -57 p.p.m.[10] for the free acid, is 98 p.p.m. This difference is significantly larger than any found for the boron trihalides. Yet, with the exception of PH_3BF_3,[24] the dissociation pressure of phosphine borane (20 cm at 0°C)[25] is greater than that of PH_3BCl_3 (0.85 cm at 0°C)[26] and PH_3BBr_3 (< 1 mm at 25°C)[26] and certainly greater than that of PH_3BI_3. If the value of -17.5 p.p.m. ($\delta_{^{11}B}$, B_2H_6)[27] is taken as a basis for calculating the mean shift difference the discrepancy is reduced but not removed. Thus, even as an indicator of adduct stability, change in chemical shift must be viewed as somewhat speculative.

Finally, as pointed out in the introduction to this chapter, the chemical shift parameters themselves are not sensitive indicators of base strength. The small and erratic changes in $\delta_{^{11}B}$ within any fixed BX_3 series exemplify this point. The chemical shift values of the mixed haloborane adducts of PH_3 and Et_3P (Table IV - 8) further accentuate this observation. A comparison of the corresponding compounds in the PH_3 and Et_3P adduct series shows nearly identical $\delta_{^{11}B}$ values, yet the two bases in question are certainly different in strength.

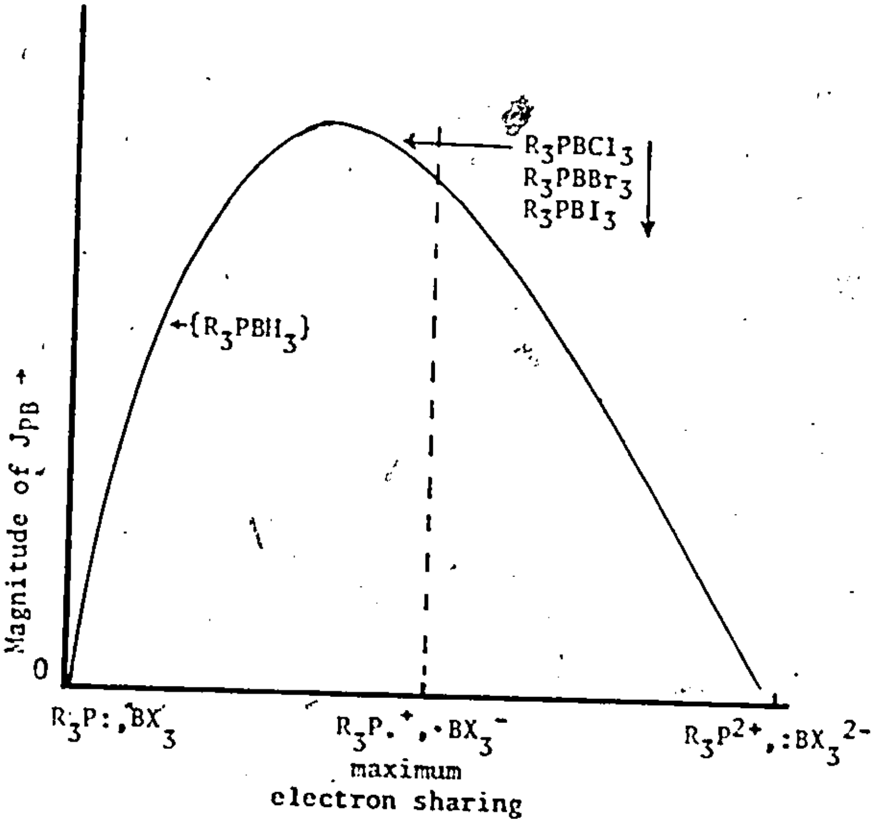
2. The Phosphorus-Boron Coupling Constant. The previously cited correlations of J_{PB} with donor basicity in $[BH_3]$ adducts[16,17] gave some promise that this parameter might, within limits, be a useful indicator of Lewis acid or base strength. While an exception to the qualitative correspondence between J_{PB} and phosphine basicity has recently been noted[28] the ^{11}B coupling constant data obtained in this investigation (Table IV - 4) are in general agreement with this correlation in that increased basicity is more marked for methyl- than for phenyl-substitution. However, when relatively small changes are involved, the absolute order of base strength as evaluated in terms of increasing J_{PB} varies somewhat when measured against different reference acids. For example, in the BI_3 adducts, the magnitude of J_{PB} would lead to the ordering of basicity as: $Me_2PH > MePH_2 > Ph_2PH > PH_3 > PhPH_2$, whereas in the BBr_3 adduct system the order would be: $Me_2PH > MePH_2 > Ph_2PH > PhPH_2 > PH_3$. The BCl_3 adduct series gives yet another set of relative basicities.

On the other hand, when the J_{PB} values of the adducts of each respective reference base are examined relative to the BX_3 series (X = Cl, Br, I) a uniform order of change is observed. Unlike J_{PH}, the J_{PB} values decrease with increasing Lewis acidity (Table IV - 4). The major contributions to the phosphorus-boron coupling constant are not clear. It is generally recognized, for instance, that when phosphine forms an adduct the orbital involved in bond formation must decrease in s-character since the other orbitals are observed to increase in s-character (as assumed on the basis of increasing J_{PH}: see Tables II - 2 and II - 6). For the acceptor species the situation is reversed upon adduct formation. As BX_3 moves from an sp^2, planar configuration to a near-tetrahedral, sp^3 configuration the bonding orbital must undergo an increase in s-character. Thus even if the Fermi contact term is an important contributor to J_{PB},[16] the opposing trends limit the predictive utility of the coupling constant.

Some insight into the significance of J_{PB} can be obtained if one considers two hypothetical extremes at which $J_{PB} = 0$: (a) no covalent interaction, R_3P:, BX_3; and (b) total electron transfer, R_3P^{2+}, $:BX_3{}^{2-}$. Between these extremes dative bond formation ($R_3P^{\delta+}:BX_3{}^{\delta-}$) leads to significant values of J_{PB} as a result of mutual sharing of electrons. Because of the opposing trends affecting the value of J_{PB} it is quite unlikely that perfect correspondence will be found between maximum contribution to J_{PB} and maximum bond strength. Figure IV - 1 qualitatively illustrates the "asymmetric" correspondence between J_{PB} and electron sharing as envisioned here. It would seem from the data of this investigation, that maximum coupling constant values are attained before maximum electron sharing. As a consequence, for the strong adducts in the series $R_nPH_{3-n}BX_3$ (R = H, Me, Ph; n = 0, 1, 2; X = Cl, Br, I), J_{PB} decreases with increasing Lewis acidity (and increasing trend toward maximum electron sharing). This decrease is paralleled by an increase in the magnitude of J_{PH} (Table II - 2). Such would be

FIGURE IV - 1

The hypothetical correspondence between the magnitude of J_{PB} and the sharing of the dative bond electrons.



expected since the BX_3 species best able to effectively generate a positive field at boron[18,19] (namely, BI_3) is the one most able to facilitate the rehybridization of the phosphine donor, and hence, bring about the largest increase in s-character in the P-H bond.

The "weaker" $R_nPH_{3-n}BH_3$ adducts might be logically placed on the left-hand portion of the hypothetical curve where neither maximum J_{PB} nor maximum donor-acceptor electron sharing have yet been attained.

Thus the weaker P-B bond is reflected in the lower J_{PB} and the lower J_{PH} values as observed in the $[BH_3]$ adducts (Tables IV - 4 and II - 2), respectively.

In only two cases was it possible to obtain J_{PB} values for BF_3 adducts. Assuming that BF_3 behaves as a BX_3 moiety rather than as $[BH_3]$, the larger J_{PB} value of Me_3PBF_3 relative to Me_3PBCl_3 is consistent with a weaker bond. The large decrease in magnitude of J_{PB} in Me_2PHBF_3 is unlikely to be related solely to a decrease in P-B bond strength. Indeed, a comparison of its J_{PH} value with that of Me_2PHBCl_3 would support this supposition (J_{PH}, Me_2PHBF_3 = 384 Hz; J_{PH}, Me_2PHBCl_3 = 420 Hz). It is more probable that a kinetic factor is dominating the process; that is, the apparent decrease in or loss of the coupling constant may be due to rapid exchange in the general process:

$$R_3P + BX_3 \rightleftarrows R_3PBX_3 \quad .$$

As a parallel to the ¹H n.m.r. investigation the mixed adduct series $Me_nPH_{3-n}BX_2Y$ and $Me_nPH_{3-n}BXY_2$ ($n = 0, 1$; $X \neq Y = Cl, Br, I$) were prepared and the ¹¹B n.m.r. spectra were recorded. Chemical shift values of the uncomplexed mixed acids[29] are listed in Table IV - 6, while chemical shifts and coupling constants for the PH_3 and $MePH_2$ adducts of the mixed acids are displayed in Table IV - 7. As with the ¹H n.m.r. parameters (APPENDIX, Section 3A) some variation in chemical shift and coupling constant values is noted for the unmixed halide components in the various combinations. This corresponds to a similar observation in the ¹H n.m.r. spectra. The methylphosphine series does however give good evidence that increasing acidity of the acceptor species is reflected in decreasing magnitude of J_{PB}. On this basis, the relative acid

TABLE IV - 6

The ^{11}B chemical shifts in p.p.m. relative to external Et_2OBF_3 for the various mixed boron trihalides, BX_2Y ($X \neq Y$ = Cl, Br, I)[29]

Boron Trihalide	$\delta_{^{11}B}$
BCl_3	-46.6
BCl_2Br	-45.4
$BClBr_2$	-42.7
BBr_3	-39.2
BCl_2I	-36.3
$BClI_2$	-18.3
BClBrI	-32.1
BBr_2I	-27.0
$BBrI_2$	-11.8
BI_3	+ 6.9

strengths may be given as: $BI_3 > BBrI_2 > BClI_2 > BCl_2I > BBr_2I > BBr_3 > BCl_2Br > BBr_2Cl > BCl_3$. Aside from a few variations, probably due to the relatively high temperature at which the spectra were recorded, this order is much the same as would be obtained on the basis of increasing magnitude of J_{PH} (Table IV - 7).

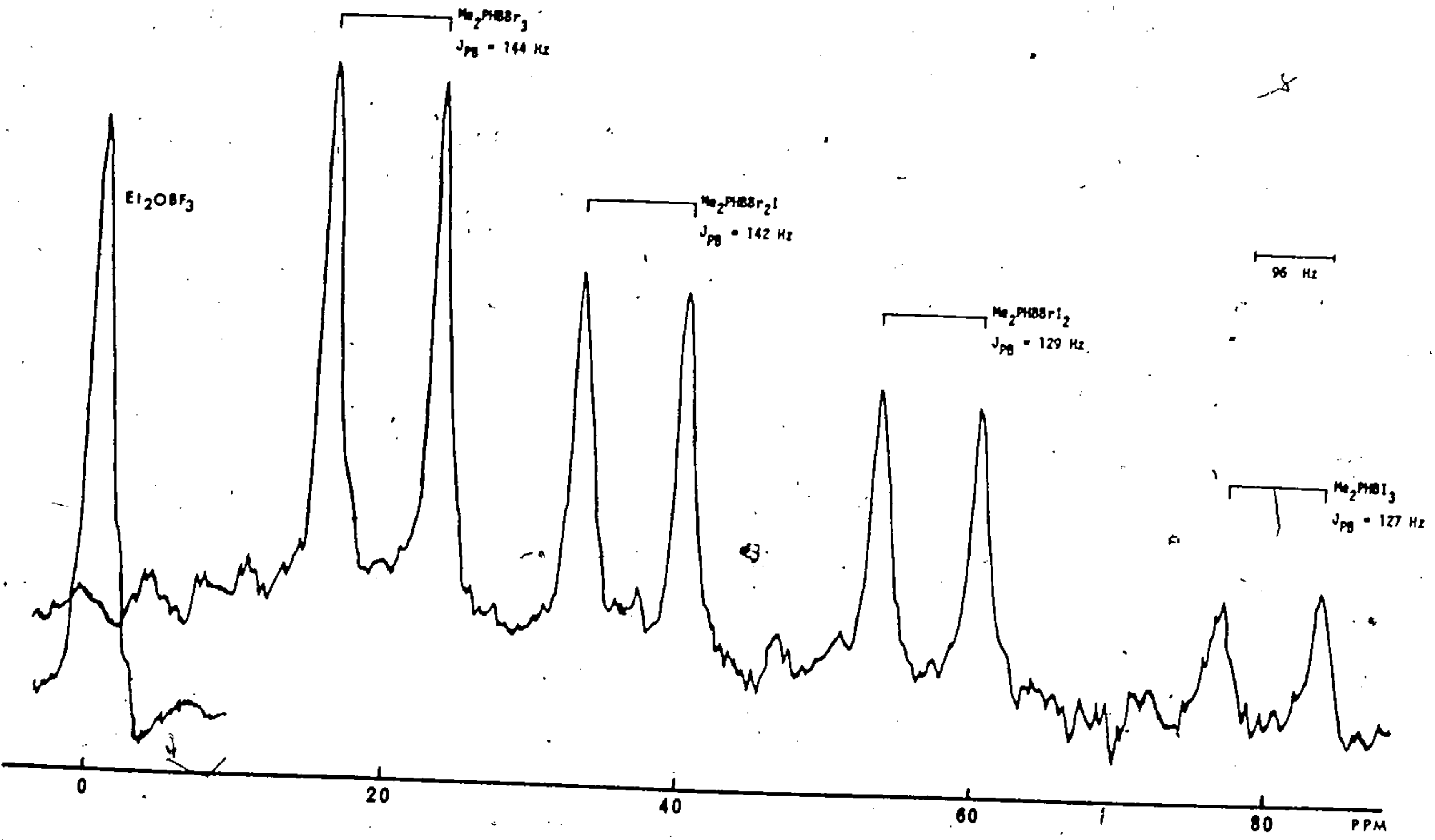
The spectrum of the $MePH_2/BBr_3/BI_3$ system recorded at -20°C in CH_3I is reproduced in Figure IV - 2. As might be expected the relative peak intensities are somewhat similar to those in the ^1H n.m.r. spectrum of the $PH_3/BBr_3/BI_3$ system (Figure III - 1, p. 70).

TABLE IV - 7

The observed ^{11}B n.m.r. parameters (δ in p.p.m. ± 1 p.p.m. relative to external Et_2OBF_3; J_{PB} in Hz ± 5 Hz) and J_{PH} (APPENDIX, Section 3A) for the adduct series $Me_nPH_{3-n}BX_2Y$ and $Me_nPH_{3-n}BXY_2$ (n = 0, 1; X ≠ Y = Cl, Br, I) recorded at - 20°C in CH_3I.

COMPOUND	$\delta_{^{11}B}$	J_{PB}	J_{PH}	COMPOUND	$\delta_{^{11}B}$	J_{PB}	J_{PH}
PH_3BCl_3	- 1.7	-	416	$MePH_2BCl_3$	- 1.5	149	422
PH_3BCl_2Br	+ 5.3	112	424	$MePH_2BCl_2Br$	+ 4.4	149	426
PH_3BClBr_2	+13.9	130	426	$MePH_2BClBr_2$	+11.4	151	426
PH_3BBr_3	+22.7	134	428	$MePH_2BBr_3$	+19.3	151	432
PH_3BCl_3	- 5.6	29(?)	420	$MePH_2BCl_3$	- 1.1	154	420
PH_3BCl_2I	+20.5	130	428	$MePH_2BCl_2I$	+18.4	139	424
PH_3BClI_2	+50.6	122	430	$MePH_2BClI_2$	+45.1	137	430
PH_3BI_3	+89.4	127	436	$MePH_2BI_3$	+80.6	130	434
PH_3BBr_3	+22.1	132	428	$MePH_2BBr_3$	+19.1	144	428
PH_3BBr_2I	+41.3	125	432	$MePH_2BBr_2I$	+36.1	142	430
PH_3BBrI_2	+64.0	127	434	$MePH_2BBrI_2$	+56.6	130	432
PH_3BI_3	+90.3	125	436	$MePH_2BI_3$	+80.0	127	430

Figure IV - 2 -- The ^{11}B n.m.r. Spectrum of the $MePH_2/BBr_3/BI_3$ System recorded in CH_3I at -20°C.



The erratic values observed in the PH_3 system are probably attributable, once again, to kinetic processes dominating in a system of significantly weaker adducts. The PH_3BCl_3 system especially affords a dramatic example of this phenomenon. That the adduct is undoubtedly present is attested to by various parameters: dissociation pressure at $0^{o}C$,[26] J_{PH} coupling constant relative to that of free phosphine (182 Hz),[30] and chemical shift data. In addition to the rapid making and breaking of the P-B dative bond, which would be expected to affect both J_{PB} and J_{PH}, perhaps there is another process involving halogen exchange at boron which has a major effect only on J_{PB}.

The series of mixed hydride-halide adducts, PH_3BH_2X and PH_3BHX_2, provides a group of compounds which reflect the convergence of rapid exchange processes and relatively weak donor-acceptor bonds. Each haloborane adduct was prepared separately and its spectrum was recorded. The ^{11}B n.m.r. parameters are given in Table IV - 8 together with those of the analogous triethylphosphine system, included for comparison purposes. A totally mixed system, $PH_3/BCl_3/B_2H_6$, was also prepared and the spectrum is reproduced in Figure IV - 3. The absence of J_{PB} in both PH_3BCl_3 and PH_3BHCl_2 but not in PH_3BH_2Cl or PH_3BH_3 is to be noted (Table IV - 8; Figure IV - 3).

It would seem then, in the light of the foregoing discussion, that while J_{PB} is of some utility as an indicator of relative acid strength, J_{PH} is probably more reliable.

TABLE IV - 8

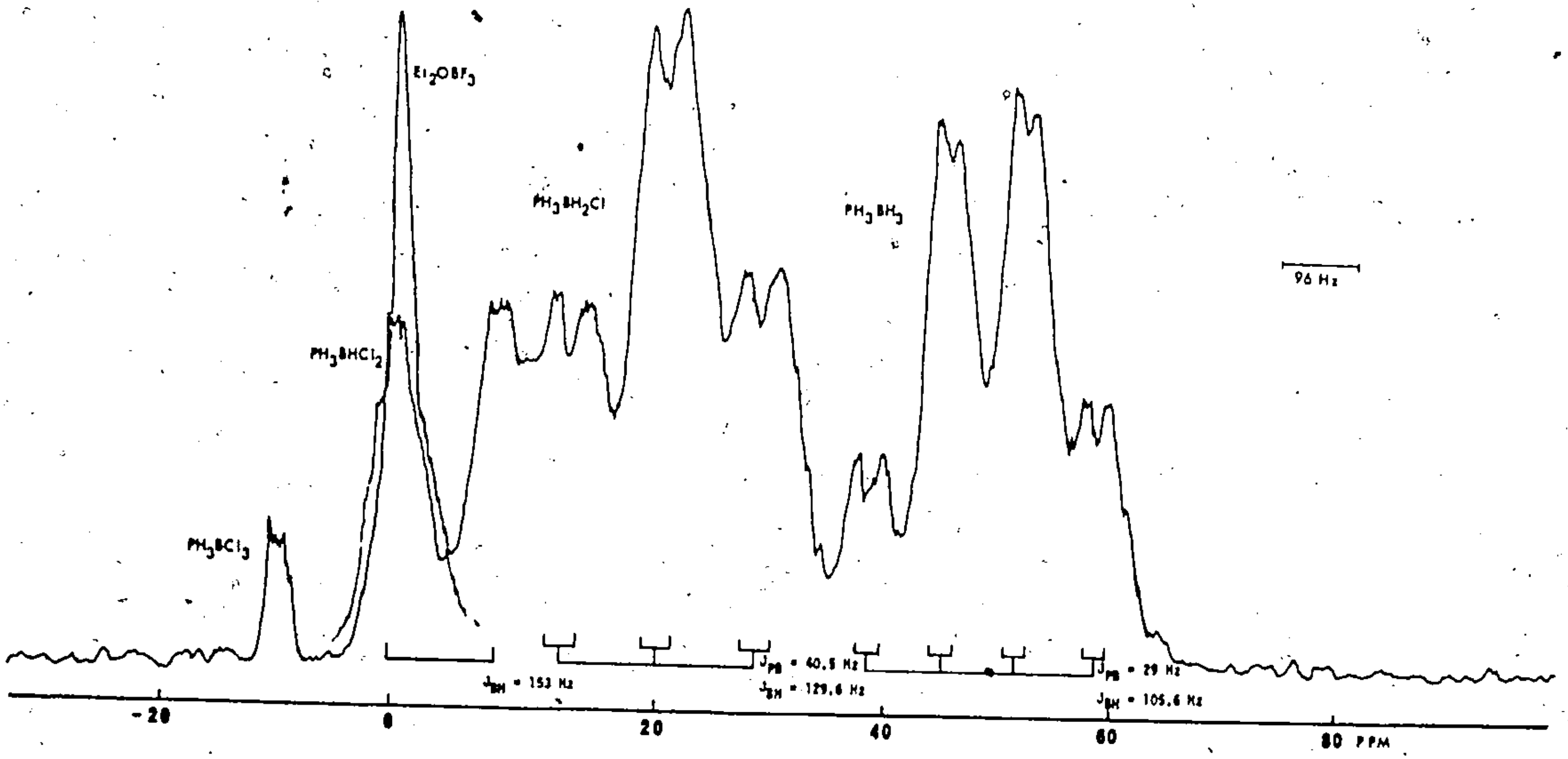
The observed ^{11}B n.m.r. parameters (δ in p.p.m. ± 1 p.p.m. relative to ext Et_2OBF_3; J_{PB} and J_{BH} in Hz ± 5 Hz) and J_{PH} (Table III - 2) for the adducts PH_3BH_2X and PH_3BHX_2 (X = H, Cl, Br, I) obtained at -20°C in CH_3I; and for the corresponding Et_3P series.[31,32]

COMPOUND	$\delta_{^{11}B}$	J_{PB}	J_{BH}	J_{PH}
PH_3BH_3[a]	+42.6	24.0	103.4	377
PH_3BH_2Cl	+19.2	41	130	395
PH_3BH_2Br	+26.5	55	130	396
PH_3BH_2I	+39.1	60	130	400
PH_3BHCl_2	+ 6.0	-	154	415
PH_3BHBr_2	+19.1	91	144	418
PH_3BHI_2	+52.4	91	154	418
Et_3PBH_3	+42	64	96	
Et_3PBH_2Cl	+20	85	115	
Et_3PBH_2Br	+25	94	111	
Et_3PBHCl_2	+ 6	131	131	
Et_3PBHBr_2	+16	<128	>128	

a) Ref. 33

3. The Boron-Hydrogen Coupling Constant. The absolute values of the direct coupling constant, J_{BH}, have been related to the π-acceptor strength of the uncomplexed phosphines.[17] No such trend is observed in the $R_nPH_{3-n}BH_3$ series (Table IV - 4) to support this concept. Further, the changes which do occur within the series are not very large (96 - 101 Hz). What is to be noted is that J_{BH} is significantly smaller in

Figure IV - 3 -- The ^{11}B n.m.r. Spectrum of the $PH_3/B_2H_6/BCl_3$ System recorded in CH_3I at -20°C.



the adducts than in free diborane (J_{BH}[terminal] = 135 Hz).[34] This supports the general concept that in its adducts [BH_3] at least approaches a tetrahedral configuration and hence has less s-character in the boron-hydrogen bonding orbitals than in B_2H_6 (HBH angle = 121°).[35]

In the series $PH_3BH_{3-n}X_n$ and $Et_3PBH_{3-n}X_n$ (X = Cl, Br, I; n = 1, 2) an increase in J_{BH} accompanies halogen substitution (contrast the J_{BH} spin-spin splitting in the spectra of $PhPH_2BH_3$ and PH_3BH_2I, Figure IV - 4). In some cases the value of J_{BH} exceeds that of the terminal protons in B_2H_6. The increase is relatively constant regardless of the nature of the halogen (Table IV - 8). This same trend is observed in the $J_{^{13}CH}$ value of the isoelectronic systems SiH_3CH_3[36] and SiH_3CH_2X[37] and in Table IV - 9 the respective coupling constant values are tabulated.

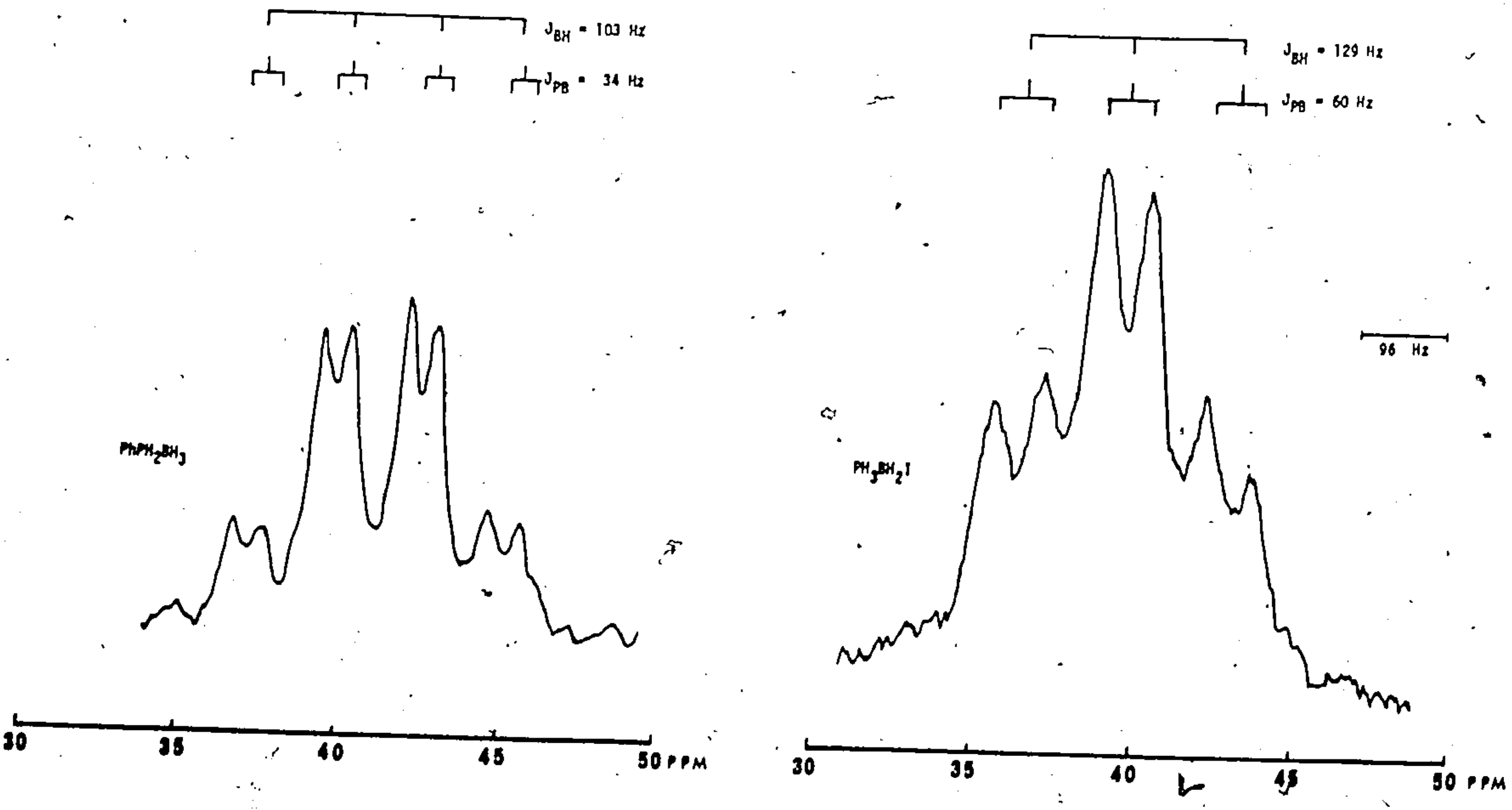
TABLE IV - 9

The coupling constants $J_{^{13}CH}$ and J_{SiH} for the isoelectronic systems Me_nSiH_{3-n} (n = 1, 2) and SiH_3CH_2X (X = Cl, Br, I).

COMPOUND	$J_{^{13}CH}$	J_{SiH}
Me_2SiH_2	122.0	190
$MeSiH_3$	122.5	194.2
SiH_3CH_2Cl	146.8	207.6
SiH_3CH_2Br	150.0	207.6
SiH_3CH_2I	149.0	205.8

Hence, this behavior is not atypical for halogen substitution and is better rationalized on the basis of a concentration of p-character in

Figure IV - 4 -- The ^{11}B n.m.r. Spectra of $PhPH_2BH_3$ and PH_3BH_2I recorded in CH_3I at 0°C.



bonds attached to more electronegative groups[38] than in terms of a trend toward planarity or an increased capacity for π-back-bonding.

REFERENCES

1. T. P. Onak, H. Landesman, R. E. Williams, and I. Shapiro, J. Phys. Chem., 63, 1533 (1959).
2. W. D. Phillips, H. C. Miller, and E. L. Muetterties, J. Amer. Chem. Soc., 81, 4496 (1959).
3. P. N. Gates, E.J. McLaughlan, and E. F. Mooney, Spectrochim. Acta, 21, 1445 (1965).
4. H. C. Brown, J. Chem. Soc., 1248 (1956).
5. P. G. Davies and E. F. Mooney, Spectrochim. Acta, 22, 953 (1966).
6. E. J. McLaughlan and E. F. Mooney, ibid., 23A, 1227 (1967).
7. A. Saika and C. P. Slichter, J. Chem. Phys., 22, 26 (1954).
8. J. R. Van Wazer, "Phosphorus and Its Compounds," Vol. I, Interscience Publishers, Inc., New York, 1958, p. 46.
9. D. R. Armstrong and P. G. Perkins, Chem. Comm., 337 (1965).
10. C. D. Good and D. M. Ritter, J. Amer. Chem. Soc., 84, 1162 (1962).
11. D. F. Gaines and R. Schaeffer, ibid., 86, 1505 (1964).
12. H. Nöth and H. Vahrenkamp, Chem. Ber., 99, 1049 (1966).
13. D. E. Young, G. E. McAchran, and S. G. Shore, J. Amer. Chem. Soc., 88, 4390 (1966).
14. M. J. Bula, D. E. Hamilton, and J. S. Hartman, J. Chem. Soc. Dalton, 1405 (1972).
15. M. J. Bula and J. S. Hartman, ibid., in press (1973).
16. R. W. Rudolph and C. W. Schultz, J. Amer. Chem. Soc., 93, 6821 (1971).
17. A. H. Cowley and M. C. Damasco, ibid., 93, 6815 (1971).
18. R. W. Rudolph and R. W. Parry, ibid., 89, 1621 (1967).
19. S. Fleming and R. W. Parry, Inorg. Chem., 11, 1 (1972).
20. J. G. Verkade, R. W. King, and C. W. Heitsch, ibid., 3, 884 (1964).
21. H. W. Myers and R. F. Putnam, ibid., 2, 655 (1963).

22. J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance," Vol. II, Pergamon Press, London, 1965, p. 973.

23. H. Landesman and R. E. Williams, J. Amer. Chem. Soc., 83, 2663 (1961).

24. E. Wiberg and U. Heubaum, Z. anorg. allgem. Chem., 225, 270 (1935); D. R. Martin and R. E. Dial, J. Amer. Chem. Soc., 72, 852 (1950).

25. E. L. Gamble and P. Gilmont, ibid., 62, 717 (1942).

26. [illegible] A. Tierney, D. W. Lewis, and D. Burg, J. Inorg. Nucl. Chem., 24, 1163 (1962).

27. [illegible] F. Gaines, R. Schaeffer, and F. Tebbe, J. Phys. Chem., 67, 1937 (1963).

28. R. Foester and K. Cohn, Inorg. Chem., 11, 2590 (1972).

29. P. N. Gates, E. F. Mooney, and D. C. Smith, J. Chem. Soc., 3511 (1964).

30. G. M. Whitesides, J. L. Beauchamp, and J. D. Roberts, J. Amer. Chem. Soc., 85, 2665 (1963).

31. J. P. Laussac, G. Jugie, and J. P. Laurent, Compt. Rend. Acad. Sc. Paris, 269C, 698 (1969).

32. G. Jugie, J. P. Laussac, and J. P. Laurent, Bull. Chim. Soc. Fr., 2542 (1970).

33. R. W. Rudolph, R. W. Parry, and C. Farran, Inorg. Chem., 5, 723 (1966).

34. D. F. Gaines, ibid., 2, 523 (1963).

35. K. Hedberg and V. Schomaker, J. Amer. Chem. Soc., 73, 1482 (1951).

36. H. Schmidbauer, Chem. Ber., 97, 1639 (1964).

37. J. Bellama and A. G. Macdiarmid, J. Organomet. Chem., 18, 275 (1969).

38. A. D. Walsh, Disc. Faraday Soc., 2, 18 (1947); H. A. Bent, Chem. Revs., 61, 275 (1961).

CHAPTER V

THE ^{31}P AND ^{19}F NUCLEAR MAGNETIC RESONANCE INVESTIGATION

INTRODUCTION

The first systematic ^{31}P n.m.r. investigation of coordination compounds with phosphine-derivative ligands was that reprted by Meriwether and Leto[1] in 1961, outlining the various factors which influence phosphorus chemical shift upon coordination.* Numerous studies have since been reported. The majority of these have been concerned with transition metal complexes of various phosphine donors. Only a relatively small number have specifically dealt with 1:1 addition compounds.[3-5] Since each of these investigations utilized boron acceptors, the data reported is especially relevant to this study and application of it will be made for purposes of comparison and completion.

^{19}F n.m.r. studies of boron trifluoride adducts of various Lewis acids have, on the other hand, been more extensively pursued. Ogg and Diehl made use of ^{19}F resonance peak broadening to study the kinetics of exchange in ROH - BF_3 systems.[6] Since then the methanol-BF_3 kinetics has been more thoroughly investigated by the same methods.[7,8] Exchange kinetics of amine-BF_3 and ether-BF_3 systems[9] as well as ketone-BF_3 systems[10] have also received attention.

A fluorine nuclear magnetic magnetic resonance investigation of

---

*Prior to this J. N. Shoolery reported the ^{31}P spectrum of Me_2PHBH_3 as part of an n.m.r. structural analysis.[2]

the free $BF_{3-n}X_n$ (X = Cl, Br; n = 0, 1, 2) species[11] revealed that the chemical shift moved to lower field as the extent of π-bonding in the molecule decreased. Thus $\delta_{^{19}F}$ of $BFBr_2$ is 130.4 p.p.m. downfield from that of BF_3. On the basis of this interpretation alone it might be expected that the ^{19}F chemical shifts of BF_3 adducts of various Lewis bases would also be downfield of the BF_3 resonance since π-bonding effects are significantly altered upon coordination. It is found however that the dominating effect accompanying adduct formation is an increase in electron density in the acceptor molecule.[12] Hence, increased shielding of the fluorine nucleus occurs upon coordination. The relative donor strength of a series of ethers was evaluated in terms of the extent of shielding of fluorine in their BF_3 adducts as: $Me_2O > MeEtO > Et_2O$.[12] Table V - 1 gives a series of Lewis bases together with the ^{19}F resonance shifts of their respective BF_3 adducts adjusted where necessary to fluorotrichloromethane, CCl_3F, as internal reference.

The system of nitrogen donors exhibits a striking correspondence between changes in chemical shift with systematic substitution in the base. It is unfortunate that this same trend is not as pronounced in other donor series. Thus in the ether series previously cited[12] the difference in chemical shift between the Me_2O and the Et_2O adducts is no greater than 1 p.p.m. at 56.45 MHz. Hartman and Gillespie[10] found that acetone, methylethylketone, methylisopropylketone, and pinacole adducts of BF_3 all have a ^{19}F resonance at +148 p.p.m. Thus it is doubtful that the ^{19}F chemical shift parameter can be consistently used to evaluate relative orders of Lewis basicity.

TABLE V-1

The ^{19}F n.m.r. parameters ($\delta_{^{19}F}$ in p.p.m. relative to int. CCl_3F; J_{BF} in Hz) for the BF_3 adducts of a series of Lewis bases.

	$\delta_{^{19}F}$	J_{BF}	Reference
BF_3	+122.5	15	10, 11
Me_3N	+164.1	15.1	13
Me_2HN	+158.8	15.5	14
MeH_2N	+152.7	15.7	14
H_3N	+146.5	13.8	14
4-MePy	+142.4	11.8	13
Me_2O	+158.2	-	15
Me_2CO	+148	-	10
H_2O	+146.6	-	16
Me_2S	+139.3	25.2	17
Me_3P	+139.0	52	14

The boron-fluorine coupling constant has been studied both in free BF_3 and in its adducts. The hyperfine boron-fluorine interaction is observed as a 1:1:1:1 quartet[11] as expected in terms of the boron nuclear spin value, $I = {}^3/_2$. The loss of J_{BF} upon the formation of some adduct systems is generally attributed to nuclear quadrupole relaxation processes occurring at the boron nucleus.[9,10,16] Rapid relaxation would cause the fluorine nuclei to experience an averaged environment of the four discrete ^{11}B spin-states, therby giving rise to a single resonance peak rather than the characteristic quartet. Only in those adducts where the electric field gradient around the boron nucleus is low are the relaxation rates slow enough to permit the existence of sufficiently long-lived ^{11}B spin states that boron-fluorine interaction with each is observable.[18] In view of the sensitivity of J_{BF} toward these phenomena, its utility as an indicator of certain chemical properties such as adduct stability or donor basicity is unlikely.

EXPERIMENTAL

1. <u>The Formation of the Adducts $R_nPH_{3-n}BH_3$ (R = Me, Ph; n = 0, 1, 2)</u>. All adducts of this series were prepared in reaction vessels D or E in the manner described in Chapter II. Phosphorus oxychloride, $POCl_3$, in small capillary tubes was used as external reference.

2. <u>The Formation of the Adducts $PH_3BH_{3-n}X_n$ (X = Cl, Br, I; n = 1, 2)</u>. These adducts were prepared in reaction vessel C in the same manner as outlined in Chapter IV. $POCl_3$ was employed as external reference.

3. <u>The Formation of the Adducts $R_nPH_{3-n}BF_3$ (R = Me, Ph; n = 0, 1, 2)</u>. The boron trifluoride adduct series was prepared in reaction vessels D or E following procedures outlined in Chapter II. Fluorotrichloromethane, CCl_3F, was used as internal standard.

RESULTS AND DISCUSSION

1. <u>The ^{31}P Spectra</u>. The low solubility of the adducts and the reduced magnetic sensitivity of the ^{31}P nucleus converged to limit the extent to which the ^{31}P n.m.r. investigation could be carried. The ^{31}P n.m.r. parameters for all [BH_3] adducts are given in Table V - 2. The parameters

TABLE V - 2

The observed ^{31}P n.m.r. parameters (δ in p.p.m. ± 2 p.p.m. relative to external $POCl_3$;† J_{PH} in Hz ± 10 Hz) for the free bases R_nPH_{3-n} (R = Me, Ph; n = 0, 1, 2) and their $[BH_3]$ adducts recorded at -20°C in CH_3I.

COMPOUND	$\delta^{31}P$	$\Delta\delta^{31}P$	J_{PH}
PH_3	+238[a]		182[d]
PH_3BH_3	+106	-132	372
$MePH_2$	+168[a]		186[d]
$MePH_2BH_3$	+ 66	-102	388
Me_2PH	+103[b]		192[d]
Me_2PHBH_3	+ 24	- 79	376 (368)[e]
$PhPH_2$	+119[c]		201[f]
$PhPH_2BH_3$	+ 46	- 73	368
Ph_2PH	+ 41[b]		239[f]
Ph_2PHBH_3	- 3	- 44	390

† All R_nPH_{3-n} literature values adjusted to external reference $POCl_3$: $\delta_{POCl_3} = \delta_{H_3PO_4} + 4$ p.p.m.

a) Ref. 20
b) Ref. 22
c) Ref. 23
d) J_{PH} values obtained from ^1H n.m.r. data, Ref. 24
e) Ref. 2
f) Ref. 25

of the free phosphines are included so that the effects of adduct formation can be clearly seen.

The chemical shifts of the free species are observed to move downfield with increasing methyl- or phenyl-substitution. The changes in

^{31}P chemical shift in trivalent phosphorus can not be properly assigned to any one particular factor such as inductive effect. Van Wazer has shown that both the paramagnetic contribution of the unbalanced 3p electrons as well as changes in bond angle around phosphorus as a function of substituent electronegativity are major contributors to chemical shift.[19]

What is of immediate interest is the pronounced downfield shift which occurs in the phosphorus resonance upon [BH_3] adduct formation. It is difficult to assess the extent to which this deshielding reflects a drift of charge from phosphorus to boron. The chemical shift difference, $\Delta\delta_{^{31}P} = \delta_{^{31}P}$ adduct - $\delta_{^{31}P}$ ligand, while large in each instance, is not constant. A consistency of $\Delta\delta_{^{31}P}$ values, paralleling the relatively constant $\Delta\delta_{^{11}B}$ values for the [BH_3] adducts, might have been expected on the basis of the previously made assumption that [BH_3] presents a similar positive field toward each ligand (Chapter IV). The lack of consistency in the $\Delta\delta_{^{31}P}$ values does not necessarily negate this assumption which implies a uniform deshielding capacity for [BH_3]. Rather, since changes in bond angles around pentavalent phosphorus are known to significantly affect ^{31}P chemical shifts[20,21] the largest $\Delta\delta_{^{31}P}$ value (PH_3 system) might very well be reflecting the greatest change in bond angle around phosphorus upon adduct formation. (Compare the HPH bond angles in PH_3BH_3 and $MePH_2BH_3$, Table II - 6, p. 57.)

The variation in $\delta_{^{31}P}$ as a function of halogen substitution at boron was also investigated using PH_3 as the donor species. The results are tabulated in Table V - 3. The only comparable series previously reported is that of the triethylphosphine adducts $Et_3PBH_{3-n}X_n$ (X = Cl,

TABLE V - 3

The observed ^1H, ^{31}P, ^{11}B n.m.r. parameters for the adducts PH_3BH_2X and PH_3BHX_2 (X = Cl, Br, I) under the conditions specified in Tables II - 2, V - 2, and IV - 4, respectively; and for the adducts Et_3PBH_2X and Et_3PBHX_2 (X = Cl, Br).[a]

	^1H		^{31}P		^{11}B	
	δ	J_{PH}	δ	J_{PH}	δ	J_{PB}
PH_3BH_3	-4.60	377	+105	372	+43	27
Et_3PBH_3			- 11	-	+42	64
PH_3BH_2Cl	-5.00	395	+104	388	+19	41
PH_3BH_2Br	-5.30	396	+101	400	+26	55
PH_3BH_2I	-5.60	400	+ 99	400	+39	60
Et_3PBH_2Cl			- 3	-	+20	85
Et_3PBH_2Br			- 3	-	+25	94
PH_3BHCl_2	-5.40	415	+ 99	416	+ 6	-
PH_3BHBr_2	-5.90	418	+ 97	424	+19	91
PH_3BHI_2	-6.30	418	+ 95(?)	424(?)	+54	91
Et_3PBHCl_2			+ 5	-	+ 6	131
Et_3PBHBr_2			+	-	+16	>128

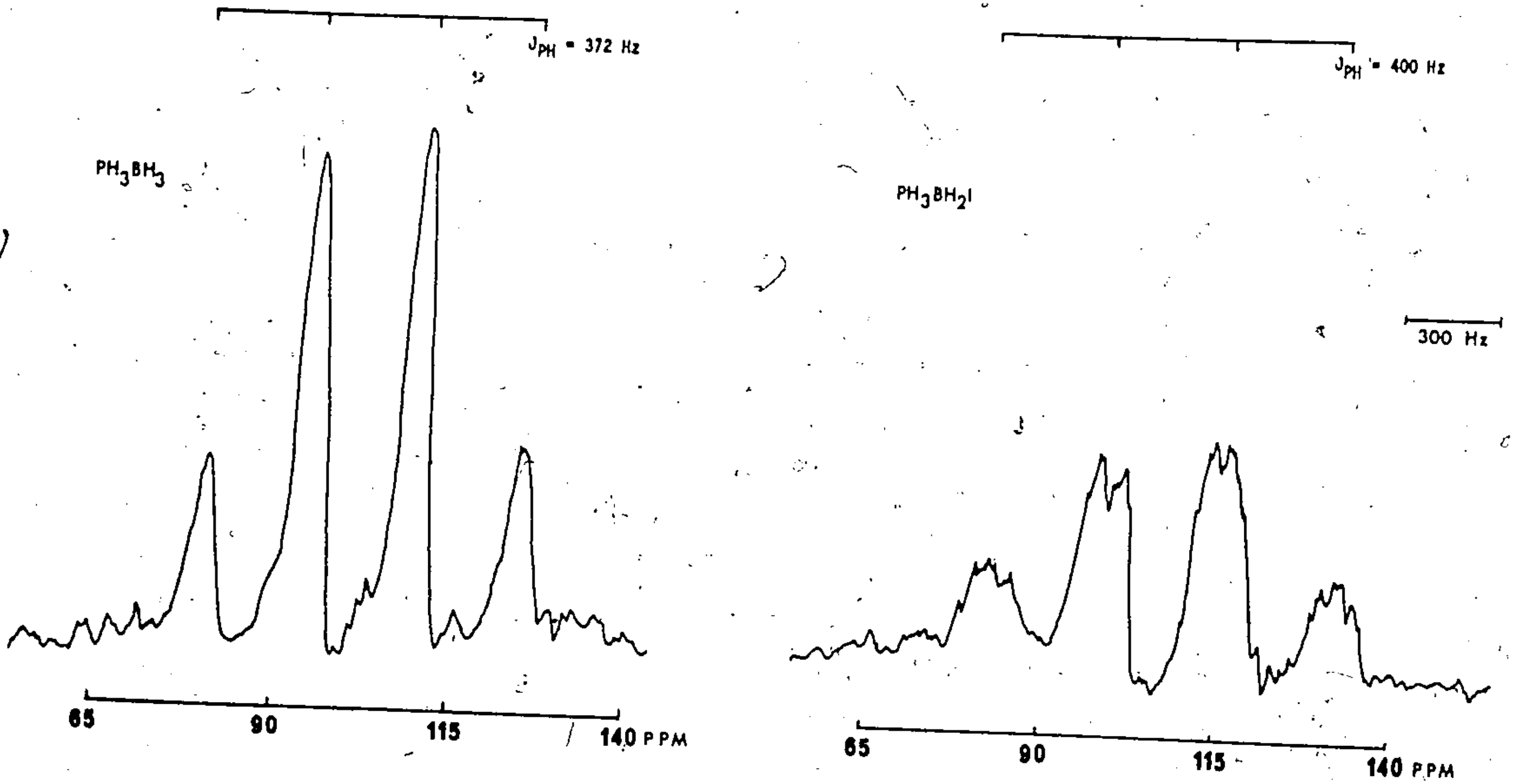
a) As taken from Refs. 4 and 5 with ^{31}P chemical shifts adjusted to external $POCl_3$ according to the equation: $\delta_{POCl_3} = \delta_{P_4O_6} - 109$ ppm.

Br;[5] n = 1, 2). Again with either base, a large change in chemical shift takes place upon coordination ($\delta_{^{31}P}$, Et_3P = +66 p.p.m.).[20] The long-range effects of halogen substitution show a relatively small downfield trend in the PH_3 adducts but an upfield trend of nearly equal magnitude in the Et_3P adduct series. The absence of consistency reflected in these minor changes is not surprising in view of the several factors which affect ^{31}P chemical shifts.

The various changes which take place in the phosphine donor, while producing substantial variations in $\delta_{^{31}P}$, apparently have little effect on $\delta_{^{11}B}$ (compare these two parameters for the corresponding adducts of the PH_3 and Et_3P series, Table V - 3). Thus "internal consistency" between the two parameters is not observed. Such would be expected only if the extent of "lone-pair" sharing were the only major contributor to both shift values.

Table V - 3 incorporates both ^1H and ^{11}B data so that adequate comparison can be made between the coupling constant parameters of all three nuclei. Thus generally good agreement is observed between J_{PH} values as obtained from ^1H and ^{31}P studies. Boron-phosphorus coupling constants could not, however, be reliably assessed from the ^{31}P spectra. Peak broadness as well as the unusually high gains required of the instrument (APPENDIX, Table 1B - 1) prevented precise measurements in this regard. The use of accumulation methods for the haloborane adducts was found to be equally unsatisfactory. Nevertheless, the increase in peak broadness along the PH_3 adduct series $[BH_3] \rightarrow BH_2X \rightarrow BHX_2$ is undoubtedly attributable to a boron-phosphorus coupling constant of increasing magnitude. Compare, for example, the width of the resonance peaks of PH_3BH_3 (J_{PB} = 29 Hz) with that of the resonance peaks of PH_3BH_2I (J_{PB} = 60 Hz) in Figure V - 1.

Figure V - 1 -- The ^{31}P n.m.r. Spectra of PH_3BH_3 and PH_3BH_2I recorded in CH_3I at -20°C.



The 1:3:3:1 quartet is, of course, common to all adducts of the phosphine haloborane series.* The spectra of $PhPH_2BH_3$ (1:2:1 triplet) and Me_2PHBH_3 (1:1 doublet) are reproduced in Figure V - 2. The varying J_{PB} values of the compounds are reflected in the widths of the phosphorus resonance peaks.

2. The ^{19}F Spectra. The ^{19}F n.m.r. parameters are displayed in Table V - 4 as a function of temperature. The enhanced solubility of the BF_3 complexes allowed the use of CH_2Cl_2 as a solvent and this permitted the recording of spectra at temperatures as low as -90°C in most cases.

The chemical shift values of the various phosphine adducts of BF_3 are in accord with expectation using Me_3PBF_3 as a basis for comparison.[14] Bearing in mind the dangers in interpreting chemical shift parameters in terms of one principal factor, it is nevertheless interesting to note that, similar to the methylamine adduct, shielding of the fluorine nucleus increases with increasing methyl-substitution. To place the various phosphines in a graduated order of basicity on the strength of this criterion might be misleading. The nearly identical chemical shift values of the phenylphosphine adducts accentuate this point. Further, it should be noted that in this latter case the chemical shift exhibits an unexpected upfield trend of a few p.p.m. when the systems are warmed. These parameters remain somewhat uncertain, especially in view of the fact that the ^1H n.m.r. spectrum of $PhPH_2BF_3$ at -70°C does not give clear indication of adduct formation (Table II - 2, p. 45).

Only the methylphosphine adducts exhibit boron-fluorine spin-spin

Figure V - 2 -- The ^{31}P n.m.r. Spectra of $PhPH_2BH_3$ and Me_2PHBH_3 recorded in CH I at -20°C.

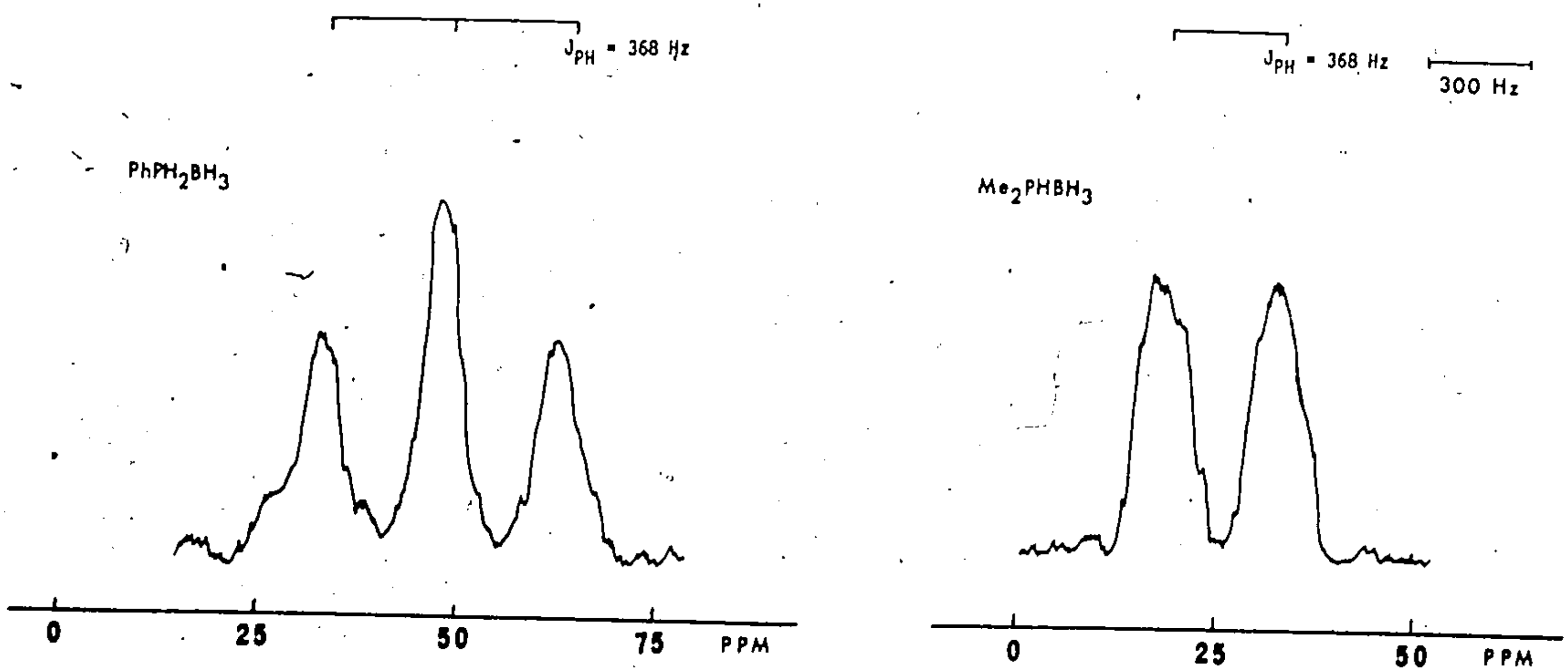


TABLE V - 4

The observed ^{19}F n.m.r. parameters (δ in p.p.m. ± 2p.p.m. relative to int. CCl_3F; J_{BF} and J_{PF} in Hz ± 10 Hz) for the adduct series $R_nPH_{3-n}BF_3$ (R = H, Me, Ph; n = 0, 1, 2) recorded at various temperatures

	PH_3BF_3			$MePH_2BF_3$			Me_2PHBF_3			$PhPH_2BF_3$			Ph_2PHBF_3		
	δ	J_{PF}	J_{BF}	δ	J_{PF}	J_{BF}	δ	J_{PF}	J_{BF}	δ	J_{PF}	J_{BF}	δ	J_{PF}	J_{BF}
-90°C	+116*	-	-	+121	300	49				+124	117	-	+125	175	-
-80	+118	-	-	+120	254	-	*			+124	-	-	+125	175	-
-70	+			+119	-	-	+135	275	54	+128			+125	150	-
-60				+119			+135	275	54	+128			+125	-	-
-50				+119			+135	275	54	+128			+130		
-40				+119			+135	275	54	+128			+130		
-30				+119			+135	275	54	+128			+130		
-20				+119			+135§	275	49	+128			+130		

* solidification of sample

+ loss of signal

§ loss of J_{BF} at -10°C; J_{PF} at 0°C.

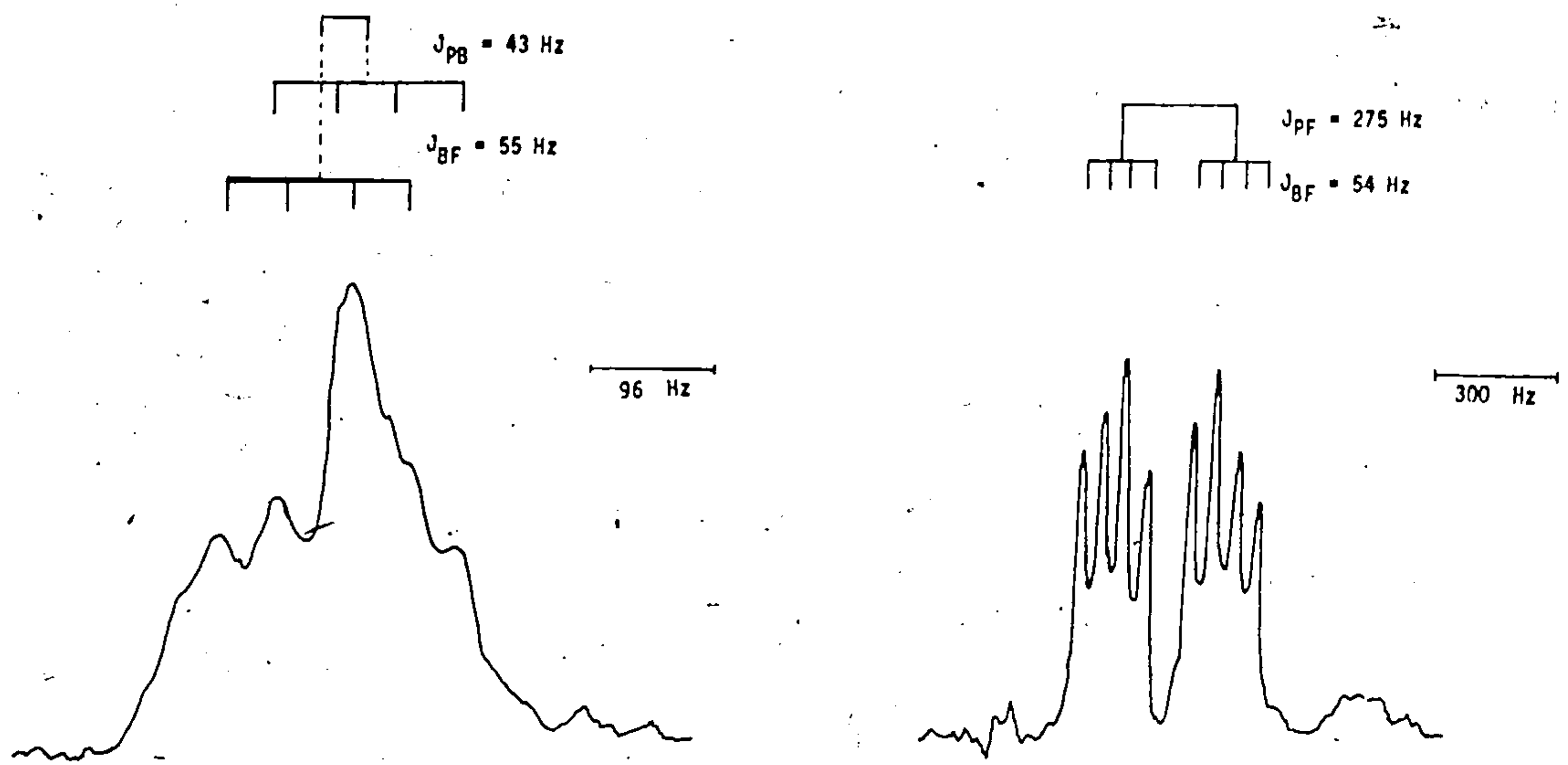
splitting, yielding the 1:1:1:1 quartet. However, of the two adducts investigated here, only in the dimethylphosphine complex is the hyperfine interaction maintained over an appreciable temperature range (Table V - 4). The absolute value of about 54 Hz for J_{BF} is comparable to that observed in the trimethylphosphine adduct (Table V - 1). A value of similar magnitude, but of less precision, was obtained from the ^{11}B n.m.r. spectrum of Me_2PHBF_3 at -30°C (Figure V - 3).

The magnitude of the indirect coupling constant, J_{PBF}, is significantly larger than that of the direct coupling constant, J_{BF}. That this should be the case is not surprising in view of the fact that the direct phosphorus-fluorine coupling constant for several compounds is observed to range from approximately 700 Hz (KPF_6 aq) to 1400 Hz (PF_3).[26] It has been pointed out[26] that the magnitude of the coupling constant is a function of the product of the respective magnetogyric ratios of the two nuclei and of a third factor related to the electronic environment in which the nuclei are immersed: $J_{AB} = \gamma_A \cdot \gamma_B \cdot f_{AB}$.* The effect of the electronic environment on the magnitude of the coupling constant is rather dramatically illustrated in the change in J_{PH} when the PH bonding orbitals of phosphine undergo an increase in s-character upon adduct formation (Chapter II). Thus only if the electronic environments about the two magnetic nuclei are nearly the same (as, for example, in two corresponding ^1H and ^2H compounds) can different J-values be attributed

---

*Since the magnetic moment, μ, is defined as $\gamma\hbar I$, if the magnitude of the hyperfine splitting were to be related to the respective magnetic moments rather than to the magnetogyric ratios, the equation for the spin-spin coupling would be: $J_{AB}I_AI_B = \mu_A \cdot \mu_B \cdot f_{AB}$. I_A and I_B are the respective nuclear spin vectors.

Figure V - 3 -- The ^{11}B and ^{19}F n.mr. Spectra of Me_2PHBF_3 recorded in CH_2Cl_2 at -20°C and -90°C, respectively.



to different nuclear moments. In the phosphorus-boron-fluorine system investigated here, the electronic environment between boron and fluorine is certainly not the same as that between phosphorus and fluorine. If it were $\frac{J_{PF}}{\gamma_P} \cdot \frac{\gamma_B}{J_{BF}} = \frac{f_{PF}}{f_{BF}} = 1$. In actual fact, this ratio is found to be significantly greater than unity.* A result other than unity, after the normalization operation indicated above, reflects the differing electronic environments through which the nuclear spins are communicated.

The eventual collapse of the quartets at -10°C is nearly coincidental with the collapse of the 1:1 doublet attributable to the indirect J_{PBF} coupling (Figure V - 4).† The almost simultaneous loss of both couplings can be accounted for on the basis of rapid exchange mechanisms. Processes involving the making and breaking of the P-B or B-F bond (or perhaps, both) may be at work in the system.

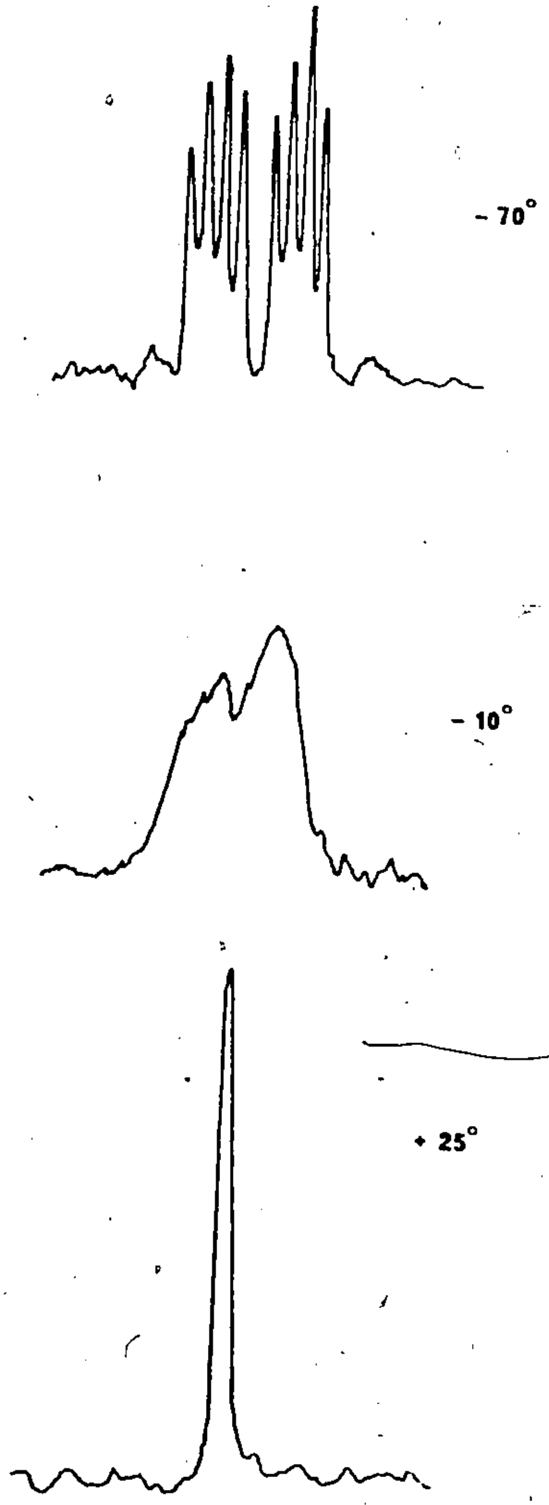
The retention of J_{BF} in the Me_2PHBF_3 system over a considerable temperature range is unique to the adduct series studied here. Its very early loss in the case of $MePH_2BF_3$ and its total absence in the spectra of the phenylphosphine adducts is best described in terms of nuclear quadrupole relaxation processes occurring at the boron nucleus as discussed earlier in this chapter. Apparently, in the dimethylphosphine system the electric field gradient around boron is relatively low.

---

* The calculated value of the ratio $\frac{275}{17.2} \times \frac{13.6}{55}$ is 3.9. The values 17.2 and 13.6 are nuclear precession frequencies in MHz at 10 kilogauss and are in the same relation as the magnetogyric ratios.[27]

† The somewhat unsymmetrical appearance of this doublet is unusual and difficult to explain.

Figure V - 4 -- The ^{19}F n.m.r. Spectrum of Me_2PHBF_3 recorded in CH_2Cl_2 at various temperatures.



Thus the relaxation time is sufficiently lengthened to permit the interaction of each ^{11}B spin state with the fluorine nuclei even at relatively high temperatures.

Hence, in the boron trifluoride adduct series, loss of J_{BF} is attributed to two different processes. In all the adducts except that of dimethylphosphine, loss of boron-fluorine coupling is ascribed to rapid relaxation processes induced by the interaction of the ^{11}B nuclear quadrupole moment with relatively high electric field gradients. But in dimethylphosphine boron trifluoride, the nearly simultaneous loss of J_{BF} and J_{PBF} clearly reflects a rapid exchange process.

The loss of J_{PBF} within the series as a function of temperature, while giving some indication of adduct stability with respect to exchange processes, does not reflect complete dissociation of the adducts because other n.m.r. parameters such as J_{PH} and $\delta_{^1H}$ (Table II - 2, p. 45) are still those of the adduct rather than of a free base.

The chemical shift of BF_3 in methylene chloride at -90°C has been reported as +122.2 p.p.m. relative to CCl_3F[10] although other values have been given.[15,28] The chemical shift for the PH_3-BF_3 system obtained in this study seems to indicate that the adduct PH_3BF_3 does not form at the temperatures specified.

REFERENCES

1. L. S. Meriwether and J. R. Leto, J. Amer. Chem. Soc., 83, 3192 (1961).
2. J. N. Shoolery, Disc. Faraday Soc., 19, 215 (1955).
3. G. Jugie, J. P. Pouyanne, and J. P. Laurent, Compt. Rend. Acad. Sc. Paris, 268C, 1377 (1969).
4. J. P. Laussac, G. Jugie, and J. P. Laurent, ibid., 269C, 698 (1969).
5. G. Jugie, J. P. Paussac, and J. P. Laurent, Bull. Chim. Soc. Fr., 2542 (1970).
6. P. Diehl and R. A. Ogg, Nature, 180, 1114 (1957).
7. P. Diehl and J. Granacher, Helv. Phys. Acta, 31, 43 (1958).
8. J. Paasivirta and S. Brownstein, J. Amer. Chem. Soc., 87, 3593 (1965).
9. S. Brownstein, A. M. Eastham, and G. A. Latremouille, J. Phys. Chem., 67, 1028 (1963).
10. R. J. Gillespie and J. S. Hartman, Canad. J. Chem., 46, 2147 (1968).
11. T. D. Coyle and F. G. A. Stone, J. Chem. Phys., 32, 1892 (1960).
12. R. A. Craig and R. E. Richards, Trans. Faraday Soc., 59, 1962 (1963).
13. B. Benton-Jones, M. E. A. Davidson, J. S. Hartman, J. J. Klassen, and J. M. Miller, J. Chem. Soc. Dalton, 2603 (1972).
14. C. W. Heitsch, Inorg. Chem., 4, 1019 (1965).
15. M. J. Bula, D. E. Hamilton, and J. S. Hartman, J. Chem. Soc. Dalton, 1405 (1972).
16. R. J. Gillespie and J. S. Hartman, Canad. J. Chem., 45, 859 (1967).
17. M. J. Bula and J. S. Hartman, J. Chem. Soc. Dalton, in press (1973).
18. J. D. Roberts, "Nuclear Magnetic Resonance," McGraw-Hill Book company, Inc., Toronto, 1959, pp. 81 - 82.
19. J. R. Van Wazer, "Phosphorus and Its Compounds," Vol. I, Interscience Publishers, Inc., New York, 1958, pp. 46 ff.
20. J. R. Van Wazer, C. F. Callis, J. N. Shoolery, and R. C. Jones, J. Amer. Chem. Soc., 78, 5715 (1956).

21. J. H. Letcher and J. R. Van Wazer, J. Chem. Phys., 44, 815 (1966).

22. K. Moedritzer, L. Maier, and L. Groenweghe, J. Chem. Eng. Data, 7, 307 (1962).

23. E. Fluck and K. Issleib, Chem. Ber., 98, 2674 (1965).

24. G. M. Whitesides, J. L. Beauchamp, and J. D. Roberts, J. Amer. Chem. Soc., 85, 2665 (1963).

25. J. W. Akitt, R. H. Craig and N. N. Greenwood, Chem. Comm., 134 (1966).

26. H. S. Gutowsky, D. W. McCall, and C. P. Slichter, J. Chem. Phys., 21, 279 (1953). J_{PF} values in Hz calculated from multiplet splittings measured in gauss.

27. J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Company, Inc., Toronto, 1959, p. 185.

28. T. D. Coyle, S. L. Stafford, and F. G. A. Stone, J. Chem. Soc., 3103 (1961).

CHAPTER VI

THE VIBRATIONAL SPECTROSCOPIC INVESTIGATION OF THE PHOSPHINE BORON TRIHALIDES

INTRODUCTION

Several infrared and Raman studies of boron trihalide adducts with a variety of donor molecules have been reported in the recent chemical literature.[1-6] Various vibrational effects attendant upon adduct formation have been the object of these studies. In addition to assigning the characteristic frequency of the donor-acceptor bond and investigating the manner in which it varies with alteration of substituents, changes in group frequencies of both donor and acceptor molecules upon adduct formahave also been investigated and interpreted. Thus, for example, it is generally observed that a significant lowering of the BX_3 asymmetric stretching frequency follows upon boron trihalide complexation.[1,2] The BX_3 symmetric stretch was originally thought to exhibit a slightly higher frequency as a result of adduct formation.[1,2] More recent studies on a variety of adducts[3-5] have, however, indicated that the BX_3 symmetric stretch in the adduct is of slightly lower frequency relative to that in the free trihalide. It has also been suggested that changes in the BH_3 stretching frequencies of borane complexes can be used as criteria of donor-acceptor bond strength, decreasing as the donor ability of the ligand increases.[6,7]

Changes in the group frequencies of the donor species do not exhibit a general trend upon adduct formation and Drago[8] recommends caution in drawing conclusions regarding the strength of Lewis acidity of acceptor molecules based on the magnitude of either positive or negative shifts in the vibrational frequencies of the donor molecule.

In the majority of spectroscopic studies pertaining to 1:1 boron trihalide adducts, the identification of the dative bond frequency and the interpretation of its variation within an adduct series have been of primary interest. These studies are best surveyed under the various donor groupings.

1. Nitrogen Donors. Nitrogen-containing Lewis bases have, by far, been most extensively used as donors toward the boron trihalides in vibrational spectroscopic studies. Parallel investigations have, on occasion, produced conflicting results or interpretations. Thus, in two separate studies of the pyridine adduct of BF_3, the N-B stretching frequency was variously assigned at 1112 cm^{-1}[9] and at 694 cm^{-1}.[3] Similar discrepancies are seen in the early spectroscopic work on H_3NBF_3,[10,11] where differences in assignment of fundamentals as well as in experimental frequencies are to be noted. Later, this same system was independently investigated by two other groups.[12,13] Both studies included work on the deuterated compound and a normal coordinate analysis. Of special note in this case is the divergence in the manner of treating the N-B stretching mode. In one report[12] νNB is specifically assigned at 738 cm^{-1} with the BF_3 asymmetric mode placed at 982 cm^{-1}. In the other study the donor-acceptor mode is interpreted as coupled with the BF_3 asymmetric stretch resulting in two new vibrational modes, one at 742 cm^{-1} and the other at 991 cm^{-1}. The rationale for this interpretation, which leads to slightly better product-rule agreement, is that the NH_3 group in the complex is of

nearly the same mass as the fluorine atoms on boron. Hence the two specified frequencies are actually mixed modes involving both B-F and N-B bond, and can be thought of as in-phase and out-of-phase stretching frequencies, respectively. The lower frequency is envisioned as a "breathing" motion, where both the nitrogen and the fluorine atoms are simultaneously moving away from boron. In the higher frequency band the boron moves in a direction opposite to that of nitrogen and the three fluorines.[14]

The foregoing illustrates the particular difficulty encountered in attempting to positively assign a fundamental frequency associated with the dative bond stretching mode. In a study of the boron trihalide complexes of trimethylamine[1] a similar difficulty was encountered. Coupling effects arising out of the interaction of other skeletal frequencies with the N-B bond rendered unambiguous assignment of a characteristic frequency very difficult. These effects must be expected whenever the acceptor or donor contains atoms heavier than hydrogen, and undoubtedly will vary as the mass characteristics of the substituents on either moiety are changed. Thus it becomes apparent that attempts to describe changes in νNB as a function of changes in one particular property such as acceptor acidity with successive halide substitution are bound to meet with much difficulty. The use of isotopically enriched varieties of adducts or of normal coordinate analysis[4] can be of some assistance in locating and assigning an "uncoupled" dative bond stretching vibration.

It is interesting to contrast the results of the above work with those of an earlier investigation of the trimethylamine and pyridine adducts of BX_3 (X = H, F, Cl, Br).[15] The assignment of the N-B stretch to a region over 1000 cm^{-1} led to the conclusion that νNB was sensitive to changes on N (νNB, pyridine complexes: 1090 - 1102 cm^{-1}; νNB, TMA complexes: 1249 - 1250 cm^{-1}) but not to changes on boron. Subsequent work with pyridine[3] and trimethylamine[12] is in basic agreement with the assignment of the N-B stretch to the 600 - 800 cm^{-1} region.[1,4,16] Table VI - 1 lists the various N-B stretching frequencies as function of the donor molecule and of the substituent on boron.

TABLE VI - 1

νNB values (cm^{-1}) reported for trivalent boron complexes of various nitrogen donors.

	$[BH_3]$	BF_3	BCl_3	BBr_3	BI_3
H_3N^a	776	738	-	-	-
$C_5H_5N^b$		692			
$C_5H_5N^c$	1090	1102	1095	1095	-
$C_5H_5N^d$			1245		
Me_3N^e		695	745	727	715
Me_3N^f	1255				
$MeCN^{g,h}$	-	645	712	706	-
Et_3N^i	645				

a) Ref. 12
b) Ref. 3
c) Ref. 15
d) Ref. 17
e) Ref. 4
f) Ref. 7
g) Ref. 23
h) Ref. 24
i) Ref. 18

Spectroscopic studies of acetonitrile complexes have been reported.[19-21] A more recent vibrational analysis, based in part on a previous crystallographic investigation,[22] was undertaken by Swanson and Shriver on the acetonitrile adduct of BF_3,[23] BCl_3 and BBr_3.[24] On the basis of force constant calculations it was concluded that the N-B bond in the BF_3 adduct was weaker than it is in the other two complexes. Using the value of the force constant as a criterion of bond strength it was found that the N-B bond in the BCl_3 and BBr_3 adducts is of nearly the same strength.

2. Oxygen Donors. Spectroscopic investigations of adducts of oxygen donors with trivalent boron have been mainly limited to infrared studies of BF_3 adducts with aldehydes,[25-27] aromatic esters,[28] and ethers.[29] Aside from the study on ether adducts, attention is mainly focused on changes in the vibrational properties of functional groups or in carbon-hydrogen stretching frequencies upon adduct formation. In the boron trifluoride-ether adduct series νOB is assigned to the 600 cm^{-1} region. The magnitude of νOB is observed to decrease as the donor strength decreases from 666 cm^{-1} for Et_2OBF_3 through 635 cm^{-1} for anisole, C_2H_5-$OCH_3 \cdot BF_3$, to 609 cm^{-1} for $BrC_2H_4OCH_3 \cdot BF_3$. By way of comparison the dative bond stretching frequency for Et_2SBF_3 is observed at 610 cm^{-1}.

3. Phosphorus Donors. The first P-B stretching frequency to have been reported was that of F_3PBH_3 by Taylor and Bissot[30] in which νPB was assigned to the 607 cm^{-1} band in the Raman spectrum. Since then a number of other reports dealing with the vibrational properties of the P-B bond have appeared. A wide range of assigned stretching frequencies is to be noted, with νPB varying from ≈400 cm^{-1} to ≈900 cm^{-1}. Most of

the compounds which have been studied are adducts of borane, [BH_3], with various phosphine donors (Table VI - 2).* With only a few exceptions, the use of the boron trihalides as acceptor species has been limited to boron trifluoride. An early investigation[36] utilized infrared techniques to obtain evidence that the adduct PH_3BCl_3 was not entirely dissociated in the gas phase. Another spectroscopic study involving BI_3 reported νPB at 550 cm^{-1} for I_3PBI_3.[37] A previous investigation of the same compound[38] reported νPB at 384 cm^{-1} and the BI_3 asymmetric stretch at 564 cm^{-1}.

TABLE VI - 2

Assigned P-B stretching frequencies (cm^{-1}) of adducts of [BH_3] and BF_3 with various phosphine donors.

	[BH_3]	BF_3	Reference
PH_3	{ 576 572		{ 32 33
$MePH_2$	564		34
Me_2PH	575		34
$EtPH_2$	562		34
Et_2PH	573		34
Ph_3P	608		35
F_3P	607		30
$(CH_3O)_3P$	799		6
$C_5H_9O_3P$	855	869	6
$C_6H_9O_3P$	860	854	6

---

*As an exception to the molecular adducts, the compound series $Ar_2B{=}PR_2$ can be cited in which νPB is assigned to 1400 cm^{-1} region.[31]

Variations in the assignment of modes other than that of the P-B interaction are also to be noted in the reports on some of these compounds. Thus in the spectrum of PH_3BH_3 the 969 cm^{-1} band is assigned to the BH_3 (e) deformation by one group[32] and to the $PH_3(a_1)$ deformation by another group.[33] Discrepancy appears as well in the assignment of stretching modes where the same band is assigned to νPH (a_1) by the former and to νBH (a_1) by the latter; yet another band is attributed to νBH (a_1)[32] and νBH (e);[33] and a third band to νBH (e)[32] and νPH (a_1).[33] Although a deuteration study[39] contributed to the clarification of these assignments, the original confusion is understandable in view of the often uncertain polarization data associated with some PH modes. Examples of this difficulty are to be seen in the results of the work described below.

Inasmuch as the spectral investigation of the PH_3BH_3 system did eventually lead to satisfactory assignments it seemed useful to extend the investigation to those boron trihalide adducts of PH_3 which were relatively stable with respect to dissociation. It was anticipated that the assignments relative to the PH_3 moiety in PH_3BH_3 and those related to BX_3 in the various nitrogen-donor adducts would be of assistance in making analogous assignments in the spectra of the new adducts.

EXPERIMENTAL

1. <u>The Formation of the Adducts</u>. All reactions were carried out in reaction vessels similar to types D and E, with a small constriction located about 5 cm. from the bottom of the tube. The procedures followed in preparing the adducts were identical to those already described

in Chapter II except that no solvent was added to the newly formed adduct prior to sealing the tube. Special care was taken to ensure complete consumption of free BX_3 by adding phosphine in measured excess. Before seal-off the system was opened to the pump for an appreciable time to remove any excess phosphine and, in the case of the PH_3BI_3 adduct, to remove any residual benzene. The deuterated analogues of the adducts were prepared using PD_3 obtained in the manner described in APPENDIX, Section 1C, 1.

2. Raman and Infrared Spectra. Raman spectra were obtained on solid samples of each adduct as well as on solutions in which CH_3I and CH_2Cl_2 were employed as solvents. The solution studies provided an opportunity for polarization measurements. Two different solvents were used so that any adduct peaks masked by the vibrational bands of one solvent would be discernable in a solution of the other solvent. The infrared spectrum of each solid adduct was recorded using CsI pellets and Nujol mulls. Solution spectra were obtained for each adduct in CH_3I and CH_2Cl_2.

The Raman spectrum of each freshly prepared adduct sealed in the 5 cm thin-walled glass tube was the first to be recorded. Following this the tube was opened under a moisture-free atmosphere and small quantities of the adduct were removed for immediate use in CsI pellets and Nujol mulls for infrared analysis. The remaining material was stored in the original glass tube, tightly capped, under a nitrogen atmosphere. Methyl iodide and methylene chloride solutions were prepared under the same conditions by dividing the material remaining into two portions and adding the appropriate solvents. A small syringe was used to transfer the clear solution to an optical cell for Raman analysis. This was tightly capped before removal from the dry box. A similar method was employed in preparing the conventional KBr solution cells for infrared analysis.

RESULTS AND DISCUSSION

The eight-atom PH_3BX_3 molecule is assumed to possess C_{3v} symmetry in staggered conformation. As a consequence of the 3n - 6 degrees of freedom for the non-linear system, eighteen normal vibrational modes are expected. Five of these will be of $\underline{a}_1$ symmetry species, one of $\underline{a}_2$, and six will be doubly degenerate $\underline{e}$ modes. All of these with the exception of the $\underline{a}_2$ will be active in both Raman and infrared, with the $\underline{a}_1$ modes being polarized and the $\underline{e}$ modes depolarized in the Raman effect. The fundamental vibrational bands for the PH_3BX_3 adducts ($H = {}^1H, {}^2H$; $X = Cl, Br, I$) are identified as indicated in Table VI - 3. The table also includes the symmetry groups of the donor and acceptor molecules prior to adduct formation and correlates the changes in vibrational symmetry species as a result of complexation.

Tables 5 - 1 through 5 - 3 of the APPENDIX contain a comprehensive listing of all vibrational data for PH_3BCl_3, PH_3BBr_3, and PH_3BI_3, respectively. Raman data on each adduct in the solid as well as for CH_3I and CH_2Cl_2 solutions of the adduct are presented. Relative band intensities and polarization data are given. All observed overtones and combination bands are included and assigned. A parallel listing of all infrared data obtained from CsI pellets and Nujol mulls of the solid as well as from solution spectra are given. A composite listing, averaging the values obtained from each method, completes the table with appropriate assignments.* A similar series of tables (Tables 5 - 4 through 5 - 6, APPENDIX) is given for PD_3BCl_3, PD_3BBr_3, and PD_3BI_3, respectively.

TABLE VI - 3

Point group classification and symmetry species of fundamental vibrational bands of PH_3, PH_3BX_3, and BX_3

PHOSPHINE		ADDUCT		BORON TRIHALIDE
C_{3v}		C_{3v}		D_{3h}
		a_1 modes		
ν_1 PH_3 st, a	↝	ν_1 PH_3 st		
ν_2 PH_3 def, a	↝	ν_2 PH_3 def		
		ν_3 PB st		
		ν_4 BX_3 st	↜	ν_1 BX_3 st, a'
		ν_5 BX_3 def	↜	ν_2 BX_3 def, a"
		a_2 mode		
		ν_6 H_3PBX_3 torsion		
		e modes		
ν_3 PH_3 st, e	↝	ν_7 PH_3 st		
ν_4 PH_3 def, e	↝	ν_8 PH_3 def		
		ν_9 BX_3 st	↜	ν_3 BX_3 st, e'
		ν_{10} PH_3 rock		
		ν_{11} BX_3 def	↜	ν_4 BX_3 def, e'
		ν_{12} BX_3 rock		

---

*In the compilation of the composite listing, Raman spectra of the solid samples were given dominant weight since these provided the most intense bands as well as the clearest overtone and combination data.

The rather good agreement between solid and solution Raman and infrared spectra suggest only a minimal influence due to torsional and/or translational lattice modes in the solid samples. While relative band intensities as well as peak broadness[40] were of some assistance in determining symmetry type, polarization data obtained from Raman spectra of the solutions were used whenever possible in assigning symmetry species. Attention was given to infrared band intensities as corroborating evidence for the validity of assignments based on the Raman data.

Although the Raman spectra give little, if any, evidence of free BX_3, the solution spectra in both techniques contained small bands attributable to free boron trihalide in PH_3BCl_3 and (to a lesser extent) in PH_3BBr_3. This is not surprising in view of the relatively high dissociation pressure associated with these weak adducts.[36]

1. The Phosphine Frequencies. The assignments for the five phosphine fundamental vibrations of each of the six adducts are recorded in Table VI - 4. Calculated values for each of the fundamentals, obtained by means of an independently done computer study,* are included for comparison purposes. The vibrations characteristic of the coordinated phosphine moiety in the BX_3 adducts were initially assigned on the basis of isotopic shifts upon deuteration and by comparison with the previous work on the PH_3BH_3 system.[39] Refinements were made following computer check, and comparison with the isoelectronic SiH_3CH_3 system also proved to be helpful.[41]

---

*The calculated frequencies for the fundamental vibrations of the PH_3BX_3 adducts ($H = {}^1H, {}^2H$; $X = Cl, Br, I$) were obtained by Dr. J. L. Hencher of this Department.

TABLE VI - 4

Observed and calculated PH_3 ($H = {}^1H$, ${}^2H$) group frequencies in $cm^{-1} \pm 3\ cm^{-1}$ for the adduct series PH_3BX_3 ($X = Cl, Br, I$)

	ν_1		ν_7		ν_2		ν_8		ν_{10}	
	obs	calc	obs	calc	obs	calc	obs	calc	obs	calc
PH_3BCl_3	2412	2413	2447	2446	985	992	1059	1057	560	557
PH_3BBr_3	2390	2393	2428	2426	979	981	1060*	1060	530	530
PH_3BI_3	2364	2362	2397	2397	981	985	1058	1055	492	493
PD_3BCl_3	1743	1719	1787	1765	785	768	774	759	441	429
PD_3BBr_3	1726	1705	1772	1751	760	762	760	757	428	406
PD_3BI_3	1709	1681	1752	1752	760	749	762	749	418	412

*The value 1060 cm^{-1} is the estimated position of the ν_8 absorption which is accidentally displaced to 1043 cm^{-1} by Fermi Resonance, see Figure VI - 3.

A comparison of the Raman spectrum of solid PH_3BCl_3 and its deuterated analogue (Figure VI - 1) illustrates the marked shift to lower frequencies that occurs in vibrations of the phosphine group for all adducts upon deuteration. Although isotopic shifts were basic to the identification of the fundamentals attributed to phosphine vibrations, polarization data were necessary to unambiguously distinguish between symmetric and asymmetric modes. The polarized spectra of solutions of all six adducts in two different solvent systems afforded some evidence for the assignments recorded in Table VI - 4. In the past some uncertainty existed as to the depolarization of the asymmetric deformation, ν_8, in PH_3BH_3.[32,33] The present system is no exception to this problem, but the solution spectra seem to indicate that the higher frequency deformation band is indeed the asymmetric $\underline{e}$ mode. Figure VI - 2(a) reproduces the CH_2Cl_2 solution spectrum of PH_3BCl_3 in 960 to 1160 cm^{-1} region. The spectrum shows the lower frequency band to be polarized. The somewhat doubtful depolarization of the higher frequency band is also discernable. The clear polarization of the former and the less clear depolarization of the latter give some support for the assignment of the deformation modes as indicated in Table VI - 4.

The difficulty in differentiating the two deformations can be appreciated by considering the apparent reversal of intensities of the respective bands in the Raman Effect. On the basis of band intensity alone one is led to assign the symmetric deformation to the higher frequency vibration. This would be in accord with the usual intensity pattern (compare, for example, the intensities of the asymmetric and

Figure VI - 1 -- The Raman Spectrum of (a) solid PD_3BCl_3 and (b) solid PH_3BCl_3.

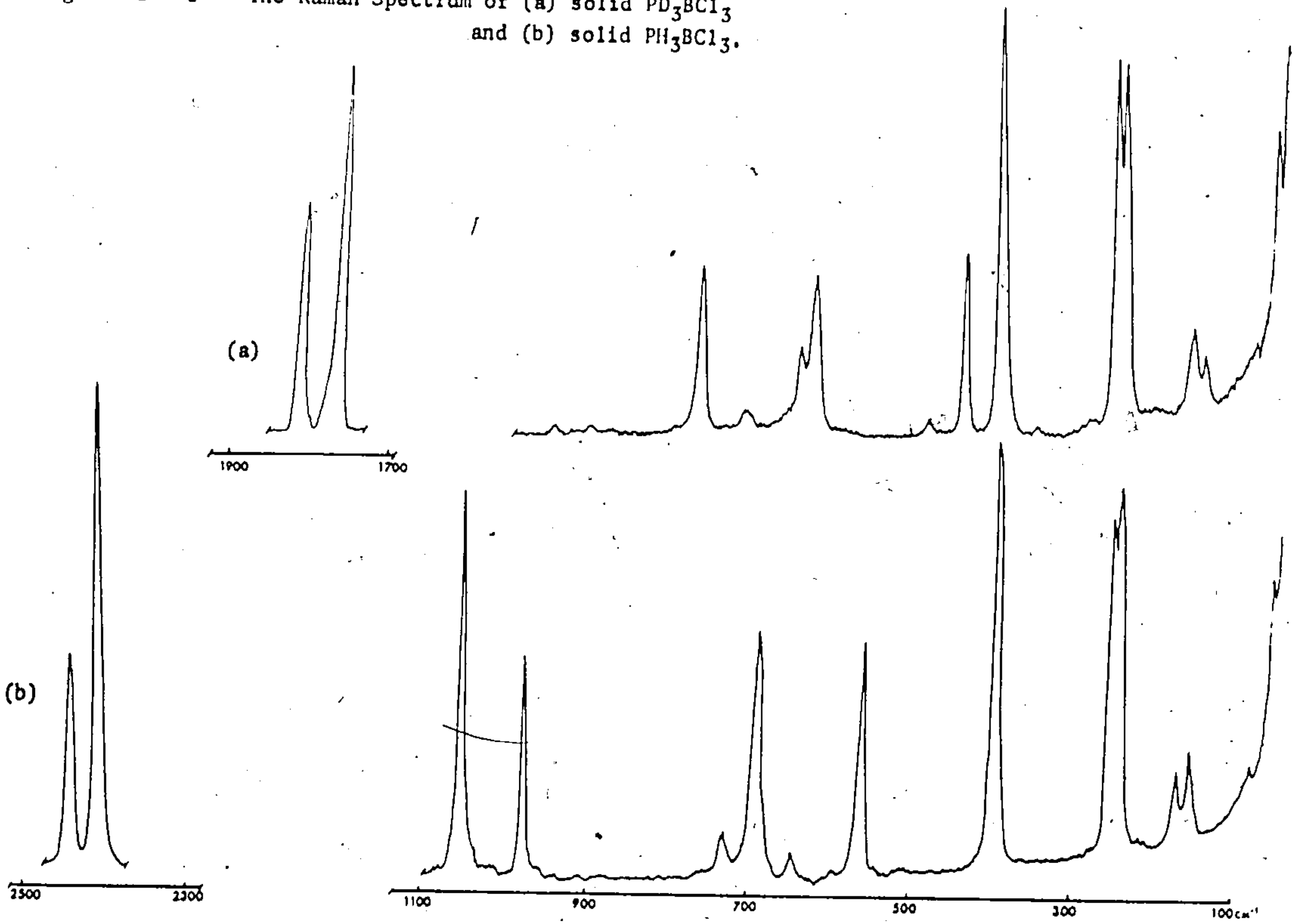
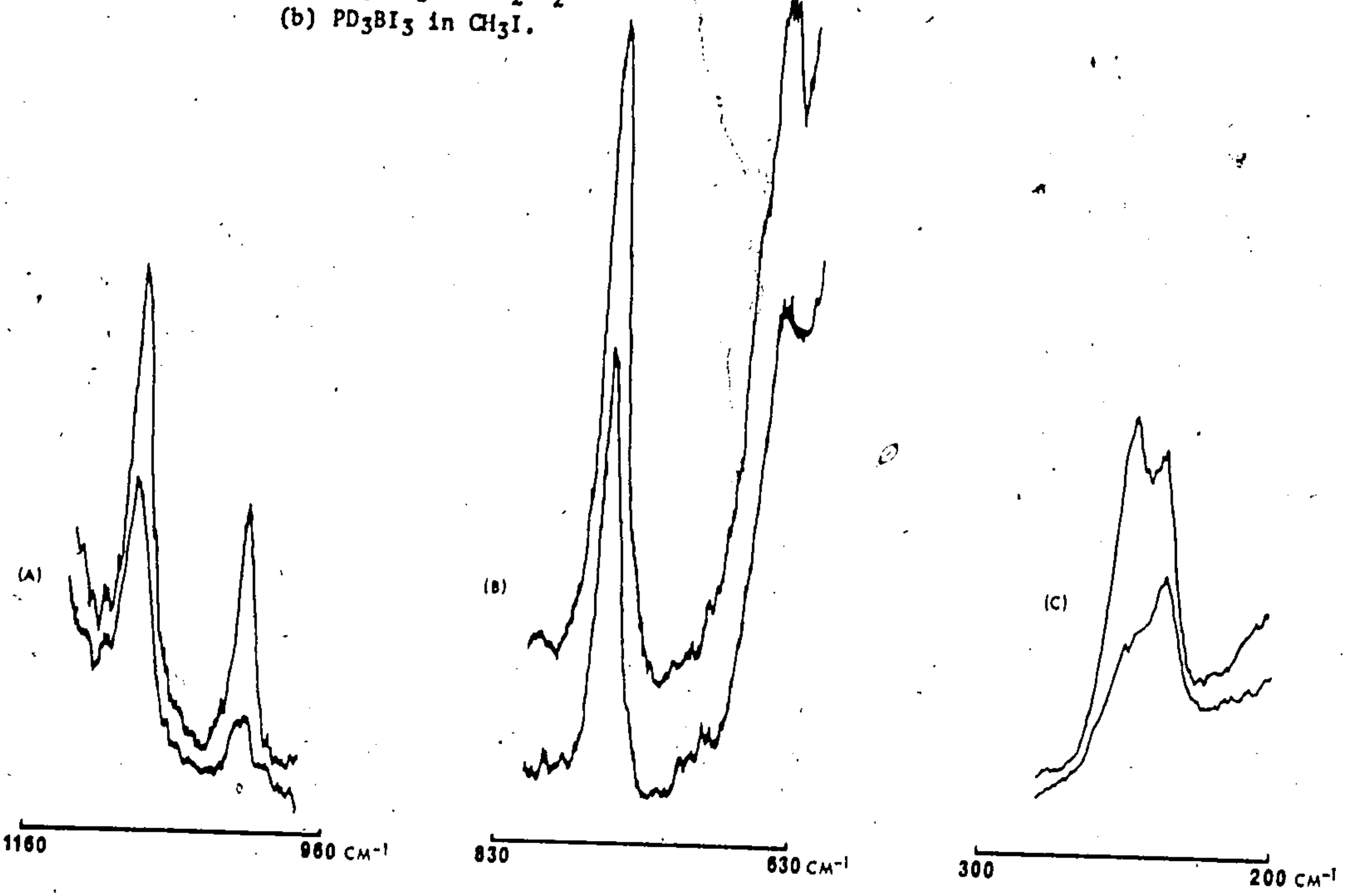


Figure VI - 2 -- Selected Regions of the Raman Spectrum of
(a) and (c) PH_3BCl_3 in CH_2Cl_2
(b) PD_3BI_3 in CH_3I.



symmetric stretching modes in the PH_3BCl_3 Raman spectrum, Figure VI -1). Nevertheless, it would be out of accord with another normal pattern in which asymmetric modes are generally observed at higher frequencies than are symmetric modes. Exceptions to this latter behavior are, however, not difficult to find.[4,5] But in the light of the polarization evidence, together with the unequivocal assignments of the PH_3BH_3 system,[39] assignments made solely on the basis of band intensities must be ruled out. Parenthetically it might also be mentioned that assigning the asymmetric deformation to the higher frequency band maintains the order in which the corresponding fundamentals appear in free phosphine, namely, 1122 cm^{-1} and 992 cm^{-1} for the e and a modes, respectively.[42]

It is on deuteration that a cross-over of bands may perhaps occur, at least in the case of the PD_3BCl_3 adduct (Table IV - 4). For the most part, however, the near coincidence of the a and e deformation modes in the deuterated adducts makes this point difficult to demonstrate. In fact, the separation of the two bands is so slight that it is almost impossible to resolve the single adsorption envelope into two components in any of the adducts. This region of the spectrum is reproduced in Figure VI - 2b for the PD_3BI_3 adduct in CH_3I. The polarized peak on the side of the solvent band is assigned to the symmetric PB stretch at 642 cm^{-1}. The band at 760 cm^{-1} of uncertain polarization does show slight evidence of splitting in the Raman solution spectrum and this is a bit more pronounced in the infrared. Furthermore, the asymmetry of the envelope alters under polarization conditions. This would be expected for nearly coincidental bands, one of which is polarized and the other not.

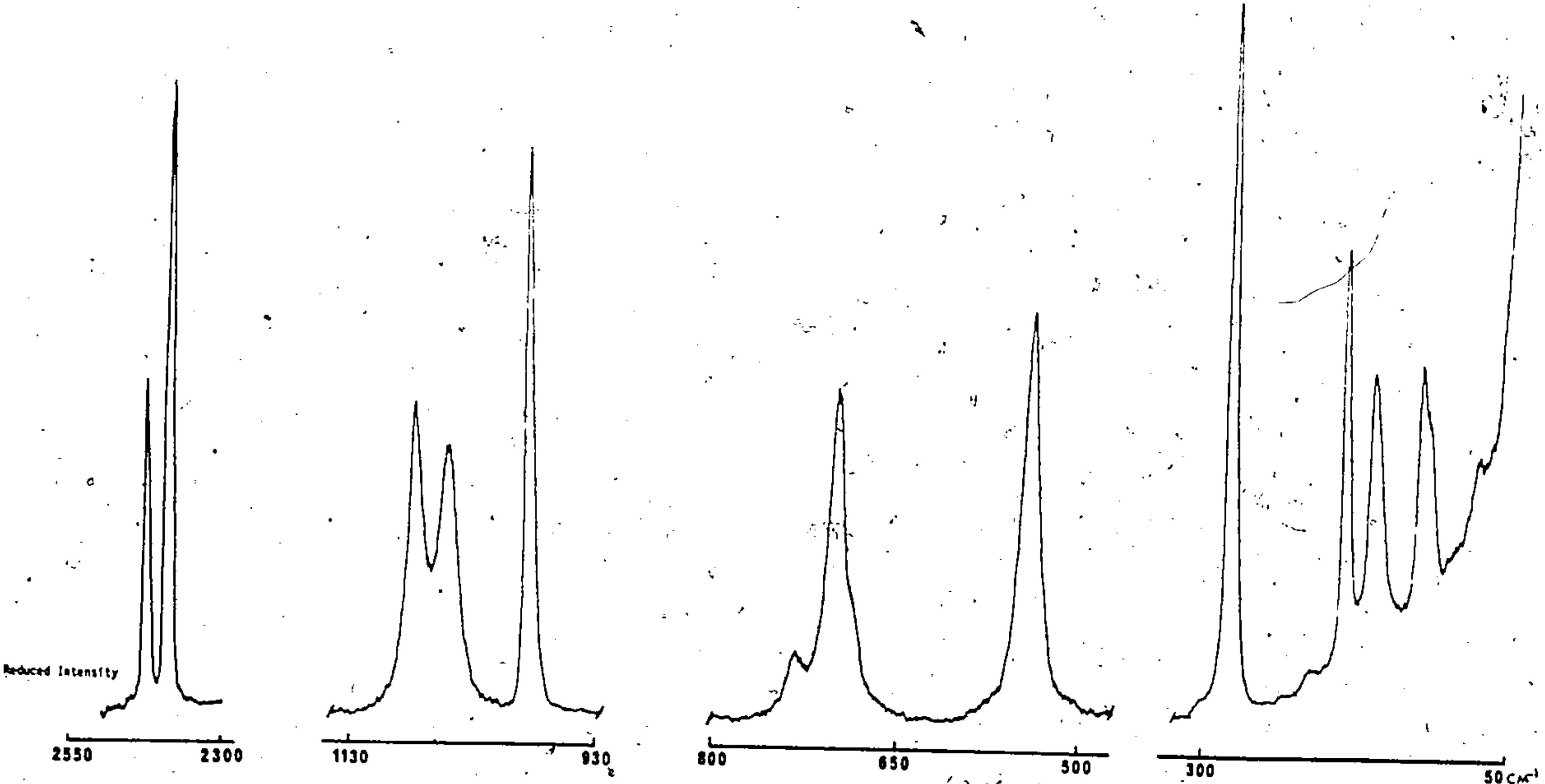
The accidental degeneracy of the two deformation modes is unusual but not without precedent. In SiH_3CH_3, both the symmetric and asymmetric SiH_3 deformations overlap to such an extent that the one band envelope can not be resolved into two distinct peaks. It is only on deuteration that both deformations are observed at different positions in the spectrum.[41] The reverse seems to be occurring in the BX_3 phosphine adducts.

Further supporting evidence for the assignment of ν_2 and ν_8 to the same envelope is seen in overtone activity. In the phosphine adducts an overtone of the symmetric deformation, $2\nu_2$, is observed at ~1950 cm^{-1}, but no $2\nu_8$ absorption is seen. In the deuterated species, an overtone assignable to ~2 x 760 cm^{-1} is apparent in the Raman spectrum of all three adducts, suggesting that ν_2 is at ~760 cm^{-1}. Further, combinations including both ν_2 and ν_8 assigned at ~760 cm^{-1} are paralleled in the protonated analogues.

Finally, the assignment of both deformations to the same position in the spectrum is also supported by the good agreement in the Teller-Redlich product rule calculations (VI - 9).

Portions of the Raman spectrum of solid PH_3BBr_3 are reproduced in Figure VI - 3. Three bands are observed in the PH_3 deformation region, 930 to 1130 cm^{-1}. The higher set provides an excellent example of Fermi resonance where an overtone and a fundamental of the same symmetry species couple to produce a decrease in the intensity of the fundamental and an increase in that of the overtone. In this case the

Figure VI - 3 -- Selected Regions of the Raman Spectrum of solid PH_3BBr_3.



asymmetric deformation, ν_8, couples with $2\nu_{10}$, the overtone of the PH_3 rocking mode at 530 cm^{-1}. In addition to a loss of intensity, the fundamental also is shifted to a frequency somewhat lower than that which would be expected on the basis of its position in the spectra of the other two adducts (Table VI - 4). This, too, is in accord with the phenomenon of Fermi resonance.[43] The Fermi resonance is observed not only in the solid, but it is clearly evident in all of the spectra of the adduct (see, for example, the infrared spectrum of PH_3BBr_3 in CH_3I, Figure VI - 4). The Fermi resonance can not be taken as additional evidence that the higher frequency PH_3 deformation is the asymmetric e mode on the ground that only bands of the same symmetry interact to yield the resonance phenomenon. By symmetry rules $2\nu_{10}$ = e x e which in turn reduces to both e and a symmetry.

The PH_3 rocking mode, ν_{10}, is a distinct band of medium intensity, depolarized in the Raman spectra of the adducts. The significant intensity of the band is a feature similar to that noted in PH_3BD_3 and PD_3BD_3[39] and for the SiH_3 rocking mode in the isoelectronic SiH_3CH_3.[41] The PH_3 rocking modes show a shift to lower frequency with increasing acidity of the acceptor species that parallels a similar trend in the PH_3 stretching modes. The trend to lower frequencies may indicate a progressive drift of charge away from the PH_3 group as the acceptor ability of the Lewis acid increases.

2. The Boron Trihalide Frequencies. The assignments of the five BX_3 fundamentals for each of the six adducts, together with calculated frequency values, are recorded in Table VI - 5. It is worthy of note

Figure VI - 4 -- Selected Regions of the Infrared Spectrum of PH_3BBr_3 in CH_3I.

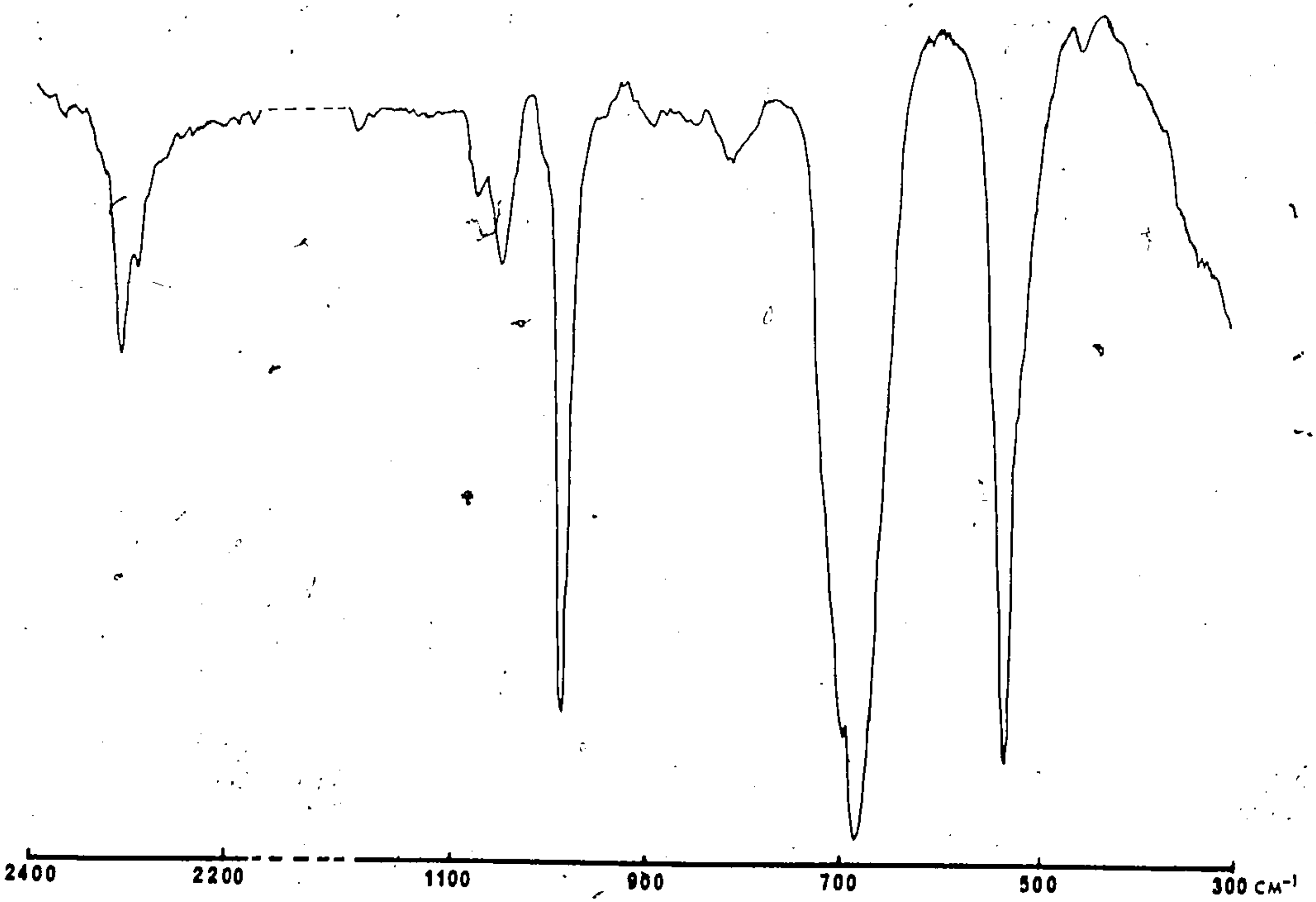


TABLE VI - 5

Observed and calculated BX_3 group frequencies in $cm^{-1} \pm 3\ cm^{-1}$ for the adduct series PH_3BX_3 ($H = {}^1H, {}^2H$; $X = Cl, Br, I$).

	ν_9		ν_4		ν_5		ν_{11}		ν_{12}	
	obs	calc	obs	calc	obs	calc	obs	calc	obs	calc
PH_3BCl_3	730	731	399	399	254	254	242	242	148	148
PH_3BBr_3	700	700	282	280	182	183	160	161	115	115
PH_3BI_3	675	676	230	228	134	135	127	126	89	89
PD_3BCl_3	718	712	395	395	247	247	238	230	144	148
PD_3BBr_3	663	677	278	272	181	181	150	153	112	115
PD_3BI_3	596	597	220	220	133	132	123	119	89	89

that, except for ν_9, the asymmetric BX_3 stretch, deuteration of the phosphine end of the adduct causes only minor changes in the BX_3 vibrational frequencies. Hence, appreciable coupling of donor and acceptor group vibrational modes does not seem to be a dominant phenomenon, and it is therefore not inappropriate to treat the vibrations of each as group frequencies.[44]

The problem of differentiating between symmetry types arises in this portion of the spectrum as well. No difficulty is experienced in identifying the BX_3 symmetric stretch, ν_4, in any of the systems. It occurs in the spectrum at a position just a little lower than where it is observed in the spectra of the free molecules.[45] Furthermore, this very intense Raman band is almost totally eliminated under polarization conditions. In addition, vibrational frequencies in the spectra of other boron trihalide adducts close to the values for ν_4 given above are assigned to the BX_3 symmetric stretch.[44,45] The asymmetric stretching mode is not so easily studied because it occurs in the 675 to 730 cm^{-1} region. This small portion of the spectrum contains a concentration of fundamental vibrational bands as well as considerable overtone and combination activity (see Figure VI - 5, the Raman spectrum of solid PD_3-BI_3). The protonated adducts are more useful in this case than the deuterated because in the spectra of the latter this difficulty is only compounded with the PD_3 deformations also occurring in this region. However, the complementarity of band intensities in the infrared and Raman is of some assistance in confirming this assignment. Thus the weak 700 cm^{-1} shoulder in the Raman spectrum of PH_3BBr_3 and the weak 596 cm^{-1} band in the Raman spectrum of PD_3BI_3 appear as very intense

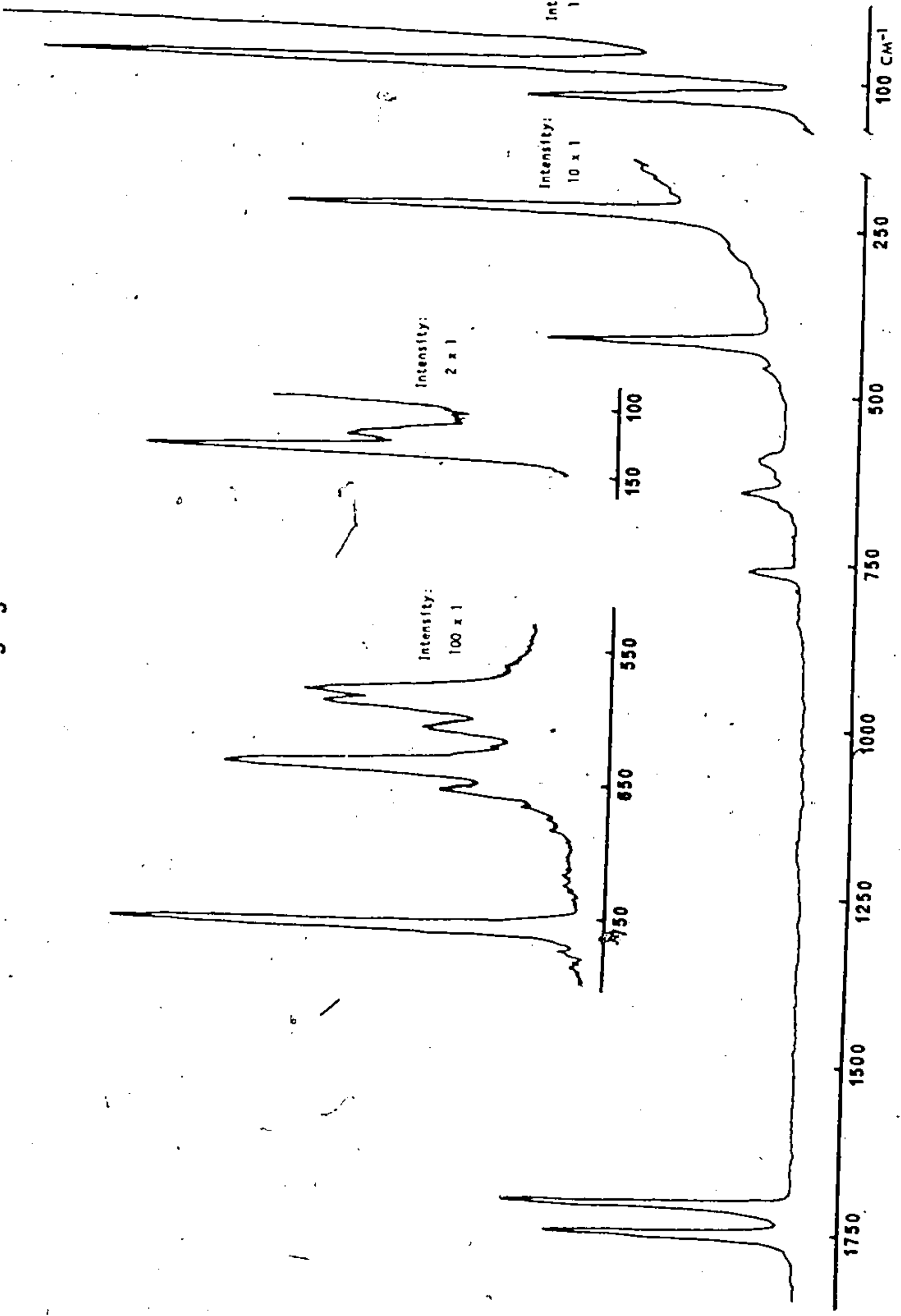
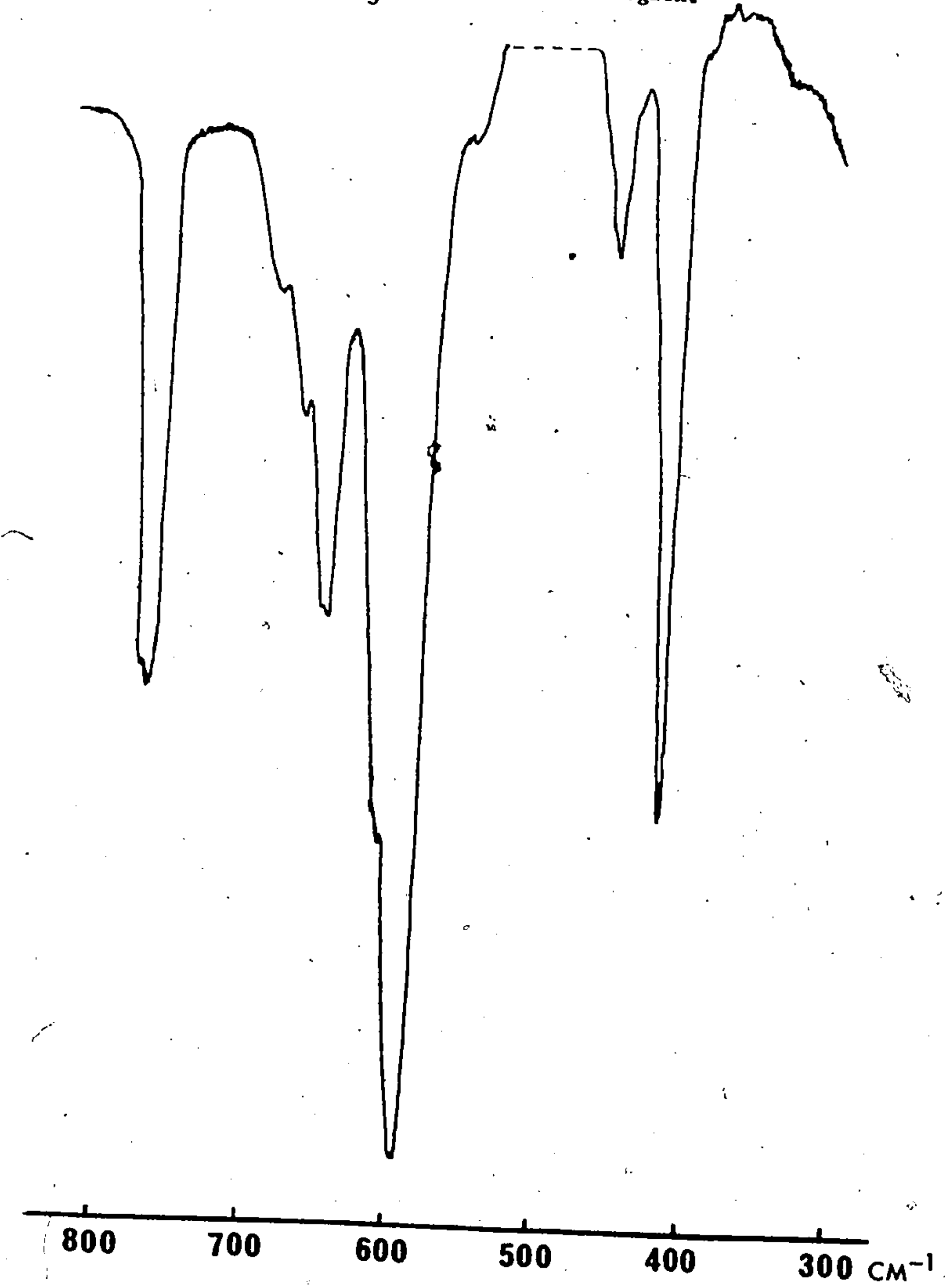


Figure VI - 5 -- The Raman Spectrum of solid PD_3BI_3.

Figure VI - 6 -- The Infrared Spectrum of PD_3BI_3 in CH_3I: 300 - 800 cm^{-1} region.



absorptions in the infrared spectra (Figures VI - 4 and VI - 6) of the respective adducts. In the spectrum of solid PD_3BI_3 the band assigned to ν_9 is clearly split indicating that in the solid state, at least, the degeneracy of the asymmetric stretching mode is partially lifted. The same behavior is noted in the protonated analogue, but to a lesser extent.

The BX_3 deformation bands ν_5 and ν_{11} occur in close proximity to one another in the spectra of all adducts, but especially in those of the BCl_3 and BI_3 compounds (Figures VI - 1 and VI - 5). The two bands are easily resolved in the spectrum of PH_3BCl_3 and the polarized Raman spectrum of this system (Figure VI - 2c) as well as those of all the adducts clearly indicate the higher wave number band to be polarized. Consequently, the higher frequency is assigned to the symmetric deformation. This is a reversal of the normal pattern and was alluded to earlier. The same reversal has been observed in other boron trihalide adduct spectra.[1,4,5] A comparison of the bands assigned to the symmetric and asymmetric BX_3 deformations in the spectrum of PH_3BBr_3 (Figure VI - 3) will reveal a significant difference in band widths, the higher being rather sharp and the lower being considerably broader. This is seen as additional evidence confirming the assignment.[40]

The BX_3 rocking mode, ν_{12}, assigned to the lowest frequency, is clearly depolarized in the Raman spectra of solutions of all the adducts. It is interesting to observe this band in the spectra of the solid species (Figures VI - 1, VI - 3, VI - 5). In both the BCl_3 and BBr_3 adducts the band exhibits some splitting. The partial lifting of degeneracy seems to be due to lattice effects in the solid since similar splitting is not observed in the solution spectra.

In a vibrational spectroscopic investigation of the boron trihalide adducts of acetonitrile,[5] the BX_3 rocking mode was assigned to a frequency higher than either of the deformation modes on the basis of normal coordinate calculations. The spectral evidence in the present study strongly favors the assignment of ν_{12} to the lowest frequency. It is to be noted that this latter assignment would also be in agreement with that of another study.[6]

3. <u>The Phosphorus-Boron Stretching Frequency</u>. The variations in the frequency of the P-B stretching mode upon deuteration or changes in the halogen species on boron are recorded in Table VI - 6.

TABLE VI - 6

The observed and calculated P-B stretching frequency, ν_3, in cm^{-1} ± 3 cm^{-1} for the adducts PH_3BX_3 ($H = {}^1H, {}^2H$; $X = Cl, Br, I$).

	BCl_3		BBr_3		BI_3	
	obs	calc	obs	calc	obs	calc
PH_3	675	674	682	685	662	662
PD_3	633	633	634	649	642	635

The P-B stretch, ν_3, is assigned to a band which is a partially polarized, medium intensity peak in the Raman spectra. This assignment places the P-B stretch somewhat higher in frequency than is observed in PH_3BH_3.[32,33] Yet it remains at a fairly constant value for all of the phosphine adducts. The relatively large shift upon deuteration is consistent with a large degree of mixing with the phosphine skeletal modes. Such mixing is not unexpected when one considers the mass of the phosphine group relative to that of the halide attached to boron. In this respect the system is quite analogous to that of H_3NBF_3 where neither the N-B mode nor the BF asymmetric stretching mode could be taken as unmixed species.[14]

The difficulty of obtaining good polarization data on the P-B stretch is demonstrated in the spectrum of PD_3BI_3 in the 630 - 830 cm^{-1} region (Figure VI -2b). The P-B stretching mode appears as a shoulder on the side of a solvent band. In spite of this less than ideal situation, the band does seem to give evidence of at least partial polarization.

It has been said that the P-B stretching frequency can be a much more sensitive criterion of bond strength than are changes in the frequencies of fundamentals of the donor or acceptor species.[6] Unfortunately, in this case, the applicability of this criterion is severely limited by overlapping fundamental bands and high overtone and combination activity. Another very important handicap to the effectiveness of this criterion as a predictive tool is the relatively large degree of mixing which occurs between the P-B stretch and other modes.

4. Overtone and Combination Bands. The Raman spectra of the solid adducts were particularly rich in overtone and combination bands. Since the symmetry species of all fundamental modes are active in both Raman and infrared, no overtone or combination band was forbidden on the basis of selection rules. Although each spectrum yielded a unique set of such

bands, a sufficient number of the same type occurred in each spectrum to warrant a compilation of this information. Tables VI - 7 and VI - 8 correlate the overtone and combination bands in the PH_3 and PD_3 adduct series, respectively. A complete listing is to be found in Tables 5 - 1 through 5 - 6 of the APPENDIX. Both types of bands were found to be particularly useful in confirming the assignment of fundamentals.

The asymmetric PH_3 stretching mode was found to be especially active in combination activity. Figure VI - 7 illustrates this activity in the 2100 - 2700 cm^{-1} region of the Raman spectrum of PH_3BBr_3. It has been pointed out that for each addition band there should be a corresponding difference band.[46] In the Raman spectra of the solid adducts this was true in most cases, although missing difference bands were occasionally expected because of the reduced intensity of these relative to the addition type combination.

Lesser overtone and combination activity was observed in the BX_3 modes. It was significant, nevertheless, as can be seen in the comprehensive listings of Section 5 of the APPENDIX.

5. Normal Coordinate Analysis and Product Rule. Further support for the assignments was sought in the application of normal coordinate analysis to the adduct systems. The calculated values for all frequencies obtained through an independently conducted normal coordinate analysis have been reported in the appropriate tables of foregoing sections. The same force constant values were used in calculating the frequencies of the deuterated analogue of each adduct as had been used in the calculations on the protonated species. The rather good agreement between observed and

TABLE VI - 7

Correlation of common overtone and combination bands for the BX_3 (X = Cl, Br, I) adducts of phosphine.

	PH_3BCl_3	PH_3BBr_3	PH_3BI_3
$\nu_7 + \nu_{11}$	2698 cm^{-1}	2585 cm^{-1}	2529 cm^{-1}
$\nu_7 + \nu_{12}$	2610	2550	2485
$\nu_7 - \nu_{12}$	2296	2318	2310
$\nu_7 - \nu_{11}$	2190	2275	2270
$2\nu_2$	1953	1947	1945
$2\nu_3$	1382	1353	1309
$2\nu_9$	1455	1384	1345
$2\nu_{10}$	1118	1071	-
$\nu_4 + \nu_5$	647	467	360

TABLE VI - 8

Correlation of common overtone and combination bands for the BX_3 (X = Cl, Br, I) adducts of phosphine-d_3.

	PD_3BCl_3	PD_3BBr_3	PD_3BI_3
$\nu_7 + \nu_{11}$	2030 cm^{-1}	1930 cm^{-1}	1879 cm^{-1}
$\nu_7 + \nu_{12}$	1938	1892	1845
$\nu_7 - \nu_{12}$	1647	1672	1662
$\nu_7 - \nu_{11}$	-	1625	1638
$2\nu_2$	1560	1516	1515
$2\nu_9$	1440	1330	1182
$2\nu_3$	1250	1287	-
$2\nu_{10}$	880	845	826

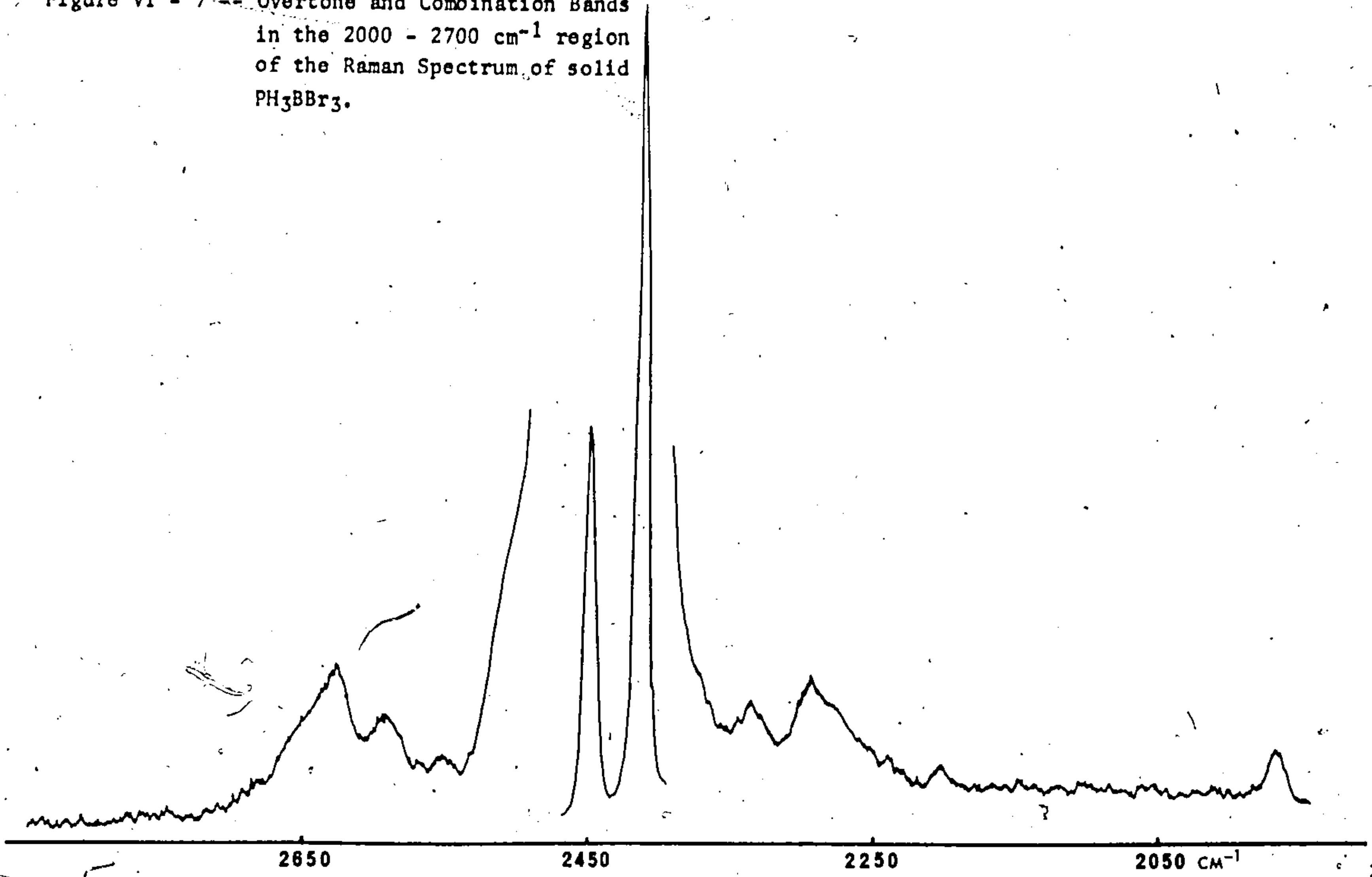


Figure VI - 7 -- Overtone and Combination Bands in the 2000 - 2700 cm^{-1} region of the Raman Spectrum of solid PH_3BBr_3.

calculated values in all six cases lends additional confidence in the correctness of the assignments.

The observed and calculated product rule ratios for each member of the series, together with the percent deviation of the experimental values, are listed in Table VI - 9.

TABLE VI - 9

Product Rule ratios for the PH_3BX_3 adducts ($H = {}^1H, {}^2H$; $X = Cl, Br, I$)

	A MODES			E MODES		
	obs	calc	percent deviation	obs	calc	percent deviation
PH_3BCl_3	0.518	0.504	2.77%	0.400	0.369	8.40%
PH_3BBr_3	0.521	0.504	3.37%	0.365	0.363	0.51%
PH_3BI_3	0.516	0.499	3.41%	0.382	0.358	6.70%

All calculated ratios were computed on the basis of the individual calculated values reported in Tables VI - 4, VI - 5, and VI - 6, using the relationship ν_D/ν_H. It is to be noted that the observed product rule ratio is slightly higher in each instance than the calculated ratio. This is in accord with expectation since the product rule ratios were not computed on the basis of corrected zero-order frequencies, ω_D/ω_H, but rather with frequencies uncorrected for anharmonicity. Since the anharmonicity factor would have less effect in the case of the adducts containing the heavier isotope, $\omega_D - \nu_D < \omega_H - \nu_H$, and the quotient $\nu_D/\nu_H = \omega_D/\nu_H$ should be slightly higher than ω_D/ω_H.[47]

REFERENCES

1. R. L. Amster and R. C. Taylor, Spectrochim. Acta, 20, 1487 (1964) and references therein.
2. A. H. Cowley and S. T. Cohen, Inorg. Chem. 4, 1200 (1965).
3. M. Taillandier and E. Taillandier, Spectrochim. Acta, 25A, 1807 (1969).
4. P. D. H. Clippard, Ph.D. Thesis, University of Michigan, 1969.
5. D. F. Shriver and B. Swanson, Inorg. Chem., 10, 1354 (1971).
6. C. W. Heitsch and J. G. Verkade, ibid., 1, 863 (1962).
7. B. Rice, R. J. Galiano, W. J. Lehmann, J. Phys. Chem., 61, 1222 (1957).
8. R. S. Drago, "Physical Methods in Inorganic Chemistry," Reinhold Publishing Co., New York, 1965, [illegible] 382.
9. H. Luther, D. Mootz, and F. Radwitz, J. prakt. Chemie, 5, 242 (1958).
10. J. Goubeau and J. Mitschelen, J. physik. Chemie, 14, 61 (1958).
11. A. A. Babuskin, J. F. Kovalev, and V. M. Emil'yanova, Opt. i Spektroskopiya, 4, 86 (1958).
12. W. Sawodny and J. Goubeau, Z. physik. Chemie, 44, 227 (1965).
13. R. C. Taylor, H. S. Gabelnick, K. Aida, and R. L. Amster, Inorg. Chem., 8, 605 (1969).
14. R. C. Taylor, "Boron-Nitrogen Chemistry," Chap. 6, Advances in Chemistry Series No. 42, American Chemical Society, 1964.
15. A. R. Katristzky, J. Chem. Soc., 2049 (1959).
16. C. L. Cluff and R. C. Taylor, Nature, 182, 390 (1958).
17. N. N. Greenwood and K. Wade, J. Chem. Soc., 1130 (1960).
18. J. N. G. Faulks, N. N. Greenwood, and J. H. Morris, J. Inorg. Nucl. Chem., 29, 329 (1967).
19. H. J. Coever and C. Curran, J. Amer. Chem. Soc., 80, 3522 (1958).
20. I. R. Beattie and T. Gilson, J. Chem. Soc., 2292 (1964).

21. K. E. Purcell and R. S. Drago, J. Amer. Chem. Soc., 88, 919 (1966).

22. B. Swanson, D. F. Shriver, and J. A. Ibers, Inorg. Chem., 8, 2182 (1969).

23. B. Swanson and D. F. Shriver, ibid., 9, 1406 (1970).

24. D. F. Shriver and B. Swanson, ibid., 10, 1354 (1971).

25. M. Rabinovitz and A. Grinwold, J. Amer. Chem. Soc., 92, 2724 (1972).

26. P. C. Myhri, C. D. Fisher, A. T. Neilsen, and W. M. Schubert, ibid., 87, 29 (1965).

27. E. Taillandier and M. Taillandier, Compt. Rend. Acad. Sc. Paris, 271B, 693 (1970).

28. M. Taillandier, J. Liquier, and E. Taillandier, J. Mol. Structure, 2, 437 (1968).

29. E. Taillandier and M. Taillandier, Compt. Rend. Acad. Sc. Paris, 263C, 1265 (1966).

30. R. C. Taylor and T. C. Bissot, J. Chem. Phys. 25, 780 (1956).

31. G. E. Coates and J. G. Livingstone, J. Chem. Soc., 1000 (1961).

32. W. Sawodny and J. Goubeau, Z. anorg. allgem. Chemie, 356, 289 (1968).

33. R. W. Rudolph, R. W. Parry, and C. F. Farran, Inorg. Chem., 5, 723 (1966).

34. J. Davis and J. E. Drake, J. Chem. Soc. (A), 2094 (1971).

35. M. A. Finch, H. G. Heal, H. Mackle, and I. O. Madden, ibid., 899 (1965).

36. P. A. Tierney, D. W. Lewis, and D. Burg, J. Inorg. Nucl. Chem., 24, 1163 (1962).

37. G. W. Chantry, A. Finch, P. N. Gates, and D. Steele, J. Chem. Soc. (A), 896 (1966).

38. A. H. Cowley and S. T. Cohen, Inorg. Chem., 4, 1200 (1965).

39. J. Davis and J. E. Drake, J. Chem. Soc. (A), 2959 (1970).

40. G. Herzberg, "Molecular Spectra and Molecular Structure," Vol. II, D. Van Nostrand Co., Inc., Princeton, New Jersey, 1968, p. 491.

41. D. F. Ball, T. Carter, D. C. McKean, and L. A. Woodward, Spectrochim. Acta, 20, 1721 (1964).

42. V. M. McConaghie and H. H. Neilsen, J. Chem. Phys. 21, 1836 (1953).

43. G. Herzberg, op. cit., p. 215; 265 ff.

44. R. S. Drago, op. cit., p. 197.

45. T. Wentink and V. H. Tiensuu, J. Chem. Phys. 28, 826 (1958).

46. J. E. Griffiths, ibid., 48, 278 (1968).

47. G. Herzberg, op. cit., p. 232.

CHAPTER VII

THE SPECTROSCOPIC INVESTIGATION -- A REVIEW

Each of the nuclear magnetic resonance studies of the phosphine borane adducts contributed uniquely to the investigation of this particular group of compounds. Proton n.m.r. data were probably the most useful and comprehensive source of information in evaluating adduct properties. This is a consequence of a combination of various factors. The relatively high sensitivity of the proton to magnetic effects compensated for the very low solubility of the adducts. Furthermore, the phosphine bases employed in this investigation, unlike several other donor molecules, all contain hydrogen directly attached to the atom through which coordination occurs. Consequently, changes in the ^1H n.m.r. parameters were very much more pronounced than when hydrogen is located at a position one atom removed from the bonding site. This constituted a significant advantage over those studies in which, for example, the chemical shifts of protons of methyl groups are investigated relative to adduct formation. In the latter case the change in $\delta_{^1H}$ is generally within 1 p.p.m. whereas in the phosphine adducts $\Delta\delta_{^1H}$ ranges from >5 to >1 p.p.m., thereby providing a clearer index in evaluating relative acceptor ability of Lewis acids. This takes on added significance in the case of small changes in the boron acceptor, as occurs in the case of mixed substituents on boron. Additional advantage lay in the magnetic spin value of the phosphorus nucleus, where $I = \frac{1}{2}$. Thus direct phosphorus-hydrogen coupling constants could be readily evaluated. The magnitude of J_{PH} also served as an indicator of relative acceptor acidities. The order of acidity obtained on the basis of J_{PH} values agrees well with that derived from ^1H chemical shift parameters, and both are in agreement with that obtained through other studies.

The effects of adduct formation on chemical shift and coupling constant are related to two dominant changes in the molecular condition of the donor species. Downfield trends in chemical shift reflect a drift of charge away from the hydrogen atoms and toward the acceptor moiety. Increased magnitude of the phosphorus-hydrogen coupling constant reflects changes in the HPH bond angle which is essentially related to the hybridization state of the phosphorus bonding orbitals. Thus both $\delta_{^1H}$ and J_{PH} served as good indicators of the acid properties of the acceptor molecule by mirroring its effects on the phosphine donor. The variation in both these parameters did not however serve as a useful guide in assessing relative orders of basicity toward a given acceptor. Nevertheless, it might be expected that these same parameters apropos the ^{11}B nucleus could furnish such a device.

The reduced sensitivity of the ^{11}B nucleus (16.5% that of ^1H)[1] added to the difficulty of this investigation since the solubility of the complexes could in no way be enhanced. All ^{11}B chemical shifts of large magnitude were found to be in a direction opposite to that in the ^1H and ^{31}P spectra and hence gave evidence of the expected shielding of the acceptor species upon adduct formation. Lesser changes in chemical shift within a donor series relative to one acceptor did not parallel those of the same series relative to a different acceptor. This somewhat erratic behavior precluded the use of ^{11}B chemical shift values in selectively ordering the Lewis bases according to donor strength.

As in the ^1H n.m.r. spectra, the nuclear spin of the phosphorus nucleus is the cause of spin-spin splitting in the ^{11}B spectra. Unfortunately, the magnitude of J_{PB} is affected by two opposing phenomena: (1) a decrease in the s-character of the phosphorus "lone pair" orbital upon coordination, and (2) a concomitant increase in the s-character of the acceptor orbital of boron. Although other factors in addition to the extent of s-character in the phosphorus-boron bond may contribute to the magnitude of J_{PB}, the Fermi contact term probably remains an important element in the spin-spin interaction. Consequently, the opposing changes in the s-character of the donor and acceptor bonding orbitals probably have a significant effect on the resultant value of J_{PB}. These opposing trends limit the predictive utility of J_{PB} in assessing various chemical properties such as P-B bond strength and donor basicity.

Solubility difficulties imposed the greatest limitation on the ^{31}P n.m.r. investigation since the magnetic sensitivity of the ^{31}P nucleus is only 6.6% that of ^1H.[1] Downfield changes of large magnitude were observed in the chemical shift of the phosphorus resonance upon adduct formation. Undoubtedly, the drift of charge from phosphorus to boron contributes to this deshielding, but the recognized sensitivity of $\delta_{^{31}P}$ to bond angle changes around phosphorus makes it difficult to determine the extent to which each factor contributes to the deshielding. When the J_{PH} values obtained from the ^{31}P investigation are compared with those of the ^1H n.m.r. study a fairly good agreement is observed.

The much smaller magnitude of J_{PB} was not resolvable from the rather broad resonance peaks of the ^{31}P spectra.

Conceptually, the ^{19}F investigation might be envisioned as analogous to the ^{1}H n.m.r. study in that fluorine is directly bonded to an atom through which coordination occurs. To a small but limited extent this idea was seen to have some validity. Thus, the chemical shift of the fluorine atom is observed to increase in an order which may parallel the increasing basicity of the donor. However, the general instability of the adducts and the lack of an independently determined order of donor basicity made it difficult to evaluate the reliability of this index. Although the direct coupling constant, J_{BF}, and the indirect constant, J_{PF}, were likewise of little help in establishing orders of basicity, they did provide an interesting study of other factors affecting the hyperfine interaction. Apparently, in the BF_3 adducts of the various phosphines, two processes are at work which both contribute to the loss of J_{BF}. In most of the adducts investigated J_{BF} is not observed because nuclear quadrupole relaxation effects result in an averaging of the four boron spin states such that no splitting of the fluorine resonance signal is observed. Only in the case of dimethylphosphine boron trifluoride is J_{BF} maintained over a considerable temperature range. In this adduct both J_{BF} and J_{PBF} are lost at a relatively high temperature and nearly simultaneously. The process at work in this case is chemical rather than nuclear -- an exchange phenomenon involving the making and breaking of either the P-B or B-F bonds, or perhaps both.

Just as changes in the magnitude of J_{PH} served as a better guide to estimating the relative strengths of the P-B bond than corresponding changes in J_{PB}, so also in the vibrational spectroscopic investigation, changes in the PH_3 stretching frequencies served as a better criterion of P-B bond strength than changes in P-B stretching frequencies. While the latter were often obscured by overlapping bands and coupled with other fundamentals, the former exhibited a gradual progression to lower frequencies as the adduct increased in stability.

Of special note, however, in this phase of the work are the assignments given for the various fundamental vibrations of the adducts. As this work was being written a report appeared concerning the vibrational spectrum of PH_3BCl_3.[2] Both infrared and Raman studies were carried out on the solid adducts. The assignments made in the report agreed only in part with those of this investigation. The divergent assignments are recorded below.

TABLE VII - 1

The PH_3 and BX_3 deformation modes (cm^{-1}) in PH_3BCl_3 ($H = {}^1H, {}^2H$) as assigned in two different investigations.

	This Work		Durig et al.[2]	
	PH_3BCl_3	PD_3BCl_3	PH_3BCl_3	PD_3BCl_3
ν_2, PH_3 sym def	985	785	1052	770
ν_8, PH_3 asym def	1059	774	977	634
ν_5, BX_3 sym def	254	247	240	240
ν_{11}, BX_3 asym def	242	238	250	250

The assignments made by Durig and co-workers are those which might be expected on the basis of band intensities or in terms of a "usual" ordering of asymmetric and symmetric modes. The limitations of both these criteria relative to the phosphine boron trihalide adducts are discussed at some length in Chapter VI. Only in this work were polarization studies carried out on solutions of all three adducts and their deuterated analogues. The assignments listed in Table VII - 1 are in keeping with the results of the polarization investigation. The good agreement between observed frequency values and those calculated on the basis of a normal coordinate analysis study helped confirm those assignments which were left in doubt by ambiguous polarization measurement.

During the course of this work several attempts were made to measure the lifetime of the P-B bond in the exchange processes associated with the adduct systems by utilizing n.m.r. methods. Similar investigations have been reported for adducts of acetonitrile and boron trihalides,[3] trimethylamine and BMe_3 and BH_3,[4] and trimethylphosphine with BMe_3.[5] Investigations of this type in which the lifetime of the P-B bond in the exchange process DA $\rightleftarrows$ D + A is measured as a function of temperature can be used to assess the activation energy of the particular bond making - bond breaking process. The quantitative information thus obtained can be employed to estimate orders of adduct stability, and donor or acceptor strength.

The procedure employed in these experiments is relatively simple. A known molar quantity of adduct is dissolved in a suitable inert solvent. A measured molar quantity of either excess acid or base is then added.

The concentrations of both the adduct and the excess reactant must be known with as much precision as possible. The resonance peaks of each species are located at different positions in the n.m.r. spectrum. Under conditions of exchange, however, when the rate of exchange between the two species is sufficiently rapid the respective resonance signals will no longer be distinct but will coalesce. This behavior is quantitatively expressed by the approximate equation:

$$\tau(\nu_A - \nu_B) = \tfrac{1}{2}\pi \quad .$$

The difference, $\nu_A - \nu_B$, corresponds to the separation of the resonance signals (measured in Hz) and τ represents the smallest time for which the two separate states of adduct and excess reactant can be distinguished.[6] The inverse of this lifetime, $1/\tau$, is the first-order rate constant of the exchange process. Thus, with the relation:

$$\frac{1}{\tau} = \pi\left(\frac{\nu_A}{2} - \frac{\nu_B}{2}\right) \quad ,$$

it becomes possible to obtain the first-order rate constant in terms of the width of the coalesced peak at half-height. This, of course, will vary with temperature, thereby providing a means of determining the first-order rate constant as a function of temperature. The Arrhenius activation energy is obtained by plotting $1/\tau$ against the inverse Kelvin temperature.[6,7] Since donor-acceptor bond lifetimes are also functionalities of concentration it is important that all concentration data be known as precisely as possible.

From the foregoing it becomes apparent that certain experimental requirements must be met if meaningful results are to be obtained from a study of this type. The solvent employed must be inert toward both adduct and excess reactant so that only exchange processes between the two will affect peak contours. The adduct, if a solid, must be sufficiently soluble even at low temperatures so that a precisely known molar quantity of it will remain in a solution of accurately measured volume. The excess reactant must have similar solubility characteristics and must have a sufficiently low vapor pressure to justify the assumption that virtually all of it remains in the solution at the operating temperatures.

In the phosphine borane adducts it quite difficult to satisfy these requirements. Of all the solvents tested, methyl iodide is best able to dissolve the adducts. However, as indicated earlier, this solvent reacts readily with the free phosphine donor. In a room temperature investigation of methyl iodide with phenylphosphine, for example, the phosphorus proton resonance peaks disappeared within 15 minutes. Benzene leaves phenylphosphine unaffected for indefinite periods, but the adducts are not sufficiently soluble in this solvent. A possible solvent system which requires additional study is iodobenzene. A preliminary investigation of its effects on free phenylphosphine showed that the free base remained intact for nearly 30 minutes at room temperature. The ability of iodobenzene to serve as a sufficiently good solvent remains to be determined. Of the various phosphine bases, phenylphosphine seems best suited for the study because of its low vapor pressure. Furthermore, the ^1H and ^{19}F n.m.r. investigations showed that the phenylphosphine adducts were most similar to those of phosphine itself in terms of stability with respect to dissociation and exchange. Hence, if activation energies for exchange mechanism of adducts of this base are obtained, reasonable estimates for those of the phosphine adducts themselves might be made.

In Chapter I brief mention was made regarding the continuing discussion concerning the extent of ionicity in the donor-acceptor bond of typical 1:1 molecular adducts. The degree to which electron transfer takes place between the bonding atoms should have a direct effect upon the manner in which the valence electrons of halogen atoms bonded to boron occupy the hybrid orbitals through which bonding occurs. Nuclear quadrupole resonance techniques may be suitable for investigating the properties of the boron-halogen bond and the changes which occur in those properties upon adduct formation. Since n.q.r. studies can be carried out on the solid adducts, no search for a suitable solvent is required, and this would indeed be a refreshing change.

REFERENCES

1. J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. I, Pergamon Press, London, 1965, p. 589.

2. J. D. Odom, S. Riethmiller, J. D. Witt, and J. R. During, Inorg. Chem., 12, 1123 (1973).

3. J. Fogelman and J. M. Miller, Canad. J. Chem., 50, 1262 (1972).

4. A. H. Cowley and J. L. Mills, J. Amer. Chem. Soc., 91, 2911 (1969).

5. K. J. Alford, E. O. Bishop, P. R. Carey, and J. D. Smith, J. Chem. Soc. (A), 2574 (1971).

6. J. H. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, 1959, p. 100.

7. T. L. Brown, Acc. Chem. Res., 1, 23 (1968).

APPENDIX

SECTION 1	Experimental Procedures
SECTION 2	^{1}H n.m.r. Data
SECTION 3	Halogen Redistribution
SECTION 4	Monoiododiborane
SECTION 5	Vibrational Spectroscopic Data

SECTION 1

EXPERIMENTAL PROCEDURES

A. EXPERIMENTAL TECHNIQUES

Several of the compounds used in this investigation are sensitive to either oxygen or moisture or both. It was necessary therefore that these be manipulated in a closed system. Such a system is provided by the standard pyrex-glass vacuum line described below. Where certain off-line procedures were required, manipulation of chemicals and equipment was effected in a nitrogen-filled dry box. The toxicity and offensive odors of some of the compounds used or synthesized also required the employment of a closed system as well as careful handling.

1. The Vacuum System. A standard high-vacuum line such as that described by Shriver[1] or Jolly[2] allowed for the most efficient handling of small gaseous samples. A system of four manifolds, each independently attached to a manometer, was joined to a central manifold. This in turn was connected to a mechanical two-stage forepump working in conjunction with an on-line mercury diffusion pump and a liquid nitrogen trap system.[3] The vacuum of the entire system was monitored by means of a Pirani gauge.[4] Each manifold was equipped with a series of taps ending in MS 19 ball-and-socket joints. The manifolds were connected in pairs by means of removable U-trap series. The trap system permitted the collection of reaction products as well as trap-to-trap distillation procedures.[5] Each trap of the four-unit series could be isolated from the others. One manifold of each pair was equipped with greaseless taps

(West-Glass Corp., Cleveland, Oh., 4 mm.) for use in those operations where the possibility of chemical attack prohibited the use of the typical greased high vacuum taps. Apiezon M or N grease was used on all standard ground glass stopcocks. The volume of each manifold was determined in a manner similar to that described by Rondeau[4] and this permitted a quantitative estimation of materials admitted to the line in terms of manometer readings (every 10 cm, approximately 1 mmole).

2. Purification of Reagents and Starting Materials. Whenever required, purification of solvents and reactants was effected by means of trap-to-trap distillation. Choice of slush bath temperature could generally be made on the basis of known or estimated melting points. Jolly[6] provides a helpful guide in the choice of slush bath in terms of melting point. Table 1 - 1 lists the slush baths and temperatures used in this investigation.

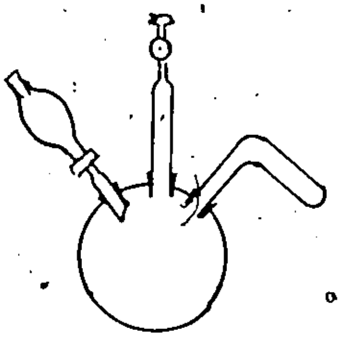
TABLE 1 - 1

A listing of slush bath components and temperatures

Bath	Temperature, °C	Bath	Temperature, °C
Ice - water	0	1-bromobutane*	-112
carbon tetrachloride*	-23	methyl cyclohexane*	-126
chlorobenzene*	-45	isopentane*	-161
CO_2 - acetone	-78	liquid nitrogen	-196
toluene*	-96		

*All materials marked with an asterisk were mixed with liquid nitrogen to bring them to the freezing point.

3. <u>Reaction and Storage Vessels</u>. Choice of taps for storage and reaction vessels was governed by experimental conditions and by the nature of the materials involved. In all experimental descriptions, reaction and storage vessels are referred to by letter identification. The following schematic provides the identification needed to clarify any procedural description.



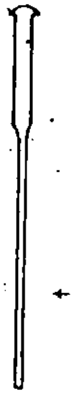
(A) 500 ml round bottom flask, Ŧ 24 - 40 equipped with tipping tube (as in the B_2H_6 preparation) or dropping funnel (as in the PD_3 preparation).

(B) Used for storage and reactions. Teflon-glass tap (Quickfit Corp., Stratfordshire, Eng.) Rotaflo 2/18. Used in reactions where internal pressure slightly exceeded atmospheric. Good for storage of reagents which attack vacuum grease, for example, BCl_3.

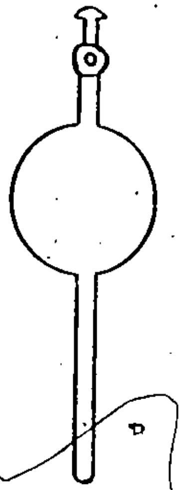
(C) Reaction vessel of same tap design as (B). Side arm joined to n.m.r. tube for transfer of reaction products prior to seal-off. Arm is packed with glass wool to serve as a filter during transfer of solutions. Sufficient space must be allowed between the n.m.r. tube and the side of the reaction vessel to permit placing a dewar vessel around one portion exclusive of the other.

(D) N.m.r. tube with constriction for seal-off connected to vacuum line Ms 19 fitting. Tap may be greased ground glass or greaseless, depending upon reaction requirements. Used in reactions involving adduct formation between gaseous reactants. Tube is pictured containing external reference capillary as in the ^{11}B and ^{31}P studies.

(E) N.m.r. tube with constriction joined to Ŧ 10 - 19 female joint. Used when substances were added to n.m.r. tube prior to attachment to the vacuum line. Male Ŧ 10 - 19 was joined to greaseless tap (G. Springham and Co., Harrow, Eng.) Viton A diaphragm.



(F) Drawn tube to capillary size used for collecting small amounts of condensible gases for n.m.r. analysis. Seal-off position is indicated by arrow between 5 - 7 cm from bottom; o.d. ca., 2 mm.



(G) Storage vessel for gases such as PH_3, B_2H_6. Volume 1 liter to 250 ml. Choice of tap is dependent upon the nature of the material stored.

B. INSTRUMENTAL TECHNIQUES

1. Nuclear Magnetic Resonance. Securing the magnetic spectra of four different nuclei required significantly different operating conditons of the instrument. These are tabulated in Table 1 - 2.

All ^1H n.m.r. spectra were obtained on a JEOL C60HL high resolution spectrometer operating at 60MHz. Tetramethylsilane was used as internal standard for all adduct spectra. External TMS was employed for the spectra of liquified gas samples in capillary tubes, Type F. Adducts were dissolved in appropriate solvent and the solutions were frozen prior to sealing the tube with a torch while still connected to the vacuum line. The instrument was periodically calibrated against a mixture of TMS and ethylbenzene. Scale settings of 9 x ½, x 1, x 2, and x 10 were checked using a standard calibrating mixture.* The normal scale setting was

---

*The seven-component mixture in CCl_4 consists of different percentages of chloroform, methylene chloride, 1,1,1-trichloroethane, p-dioxane, acetone, cyclohexane, and TMS,

TABLE 1 - 2

Typical instrument settings for recording the n.m.r. spectra of the various nuclei

	^{1}H	^{11}B	^{31}P	^{19}F
Radio Frequency, MHz	60.00	19.25	24.29	65.45
Crystal, KHz	-	13582.9	11904.4	3552.6
RF Unit, amp	3	4	5	3
RF Level, -db	36	26	16	36
FF Amplitude	0.1 x 5	1 x 2	1 x 8	1 x 5
Response	1	2	5	4
Scale Setting, p.p.m.	9 x 2	9 x 10	300	{ 300 9 x 10
Hz/mm, chart scale	3	4.8	16	{ 25 14.1
N.m.r. Lock	ON	ON	OFF	OFF @ 300 ppm

9 x 2 p.p.m. Temperatures were regulated using a JES-VT-3 temperature controller modified to function between +200 and -150°C. Occasional calibration checks of the thermocouple were made using a low temperature thermometer inserted into the probe. When a precision of ±1°C was required the instrument was calibrated using a methanol sample and the calibration curves of Van Geet.[7] Temperatures were varied from +70°C to -90°C

All ^{11}B spectra were recorded on adducts contained in sealed tubes at 19.25 MHz with Et_2OBF_3 serving as external reference. On ocassion, trimethoxyboron, $B(OMe)_3$, was employed as external reference. Instrument calibration on the 9 x 10 p.p.m. scale was effected by means of a mixture of the two references, one external to the other. Calibration was also checked by comparing chemical shifts and J_{PB} data of known compounds, for example, Me_2PHBH_3,[8] with the recorded spectrum. CH_3I was used as solvent for the adduct systems. The low solubility of these species severely reduced the intensity of the ^{11}B resonance peaks. Removal of the reference capillary partially overcame this difficulty and allowed for a more precise measurement of coupling constants. Removal was implemented by inverting the sealed tube and then carefully returning it to its original position in the probe, leaving the capillary in the upper portion of the non-spinning tube and out of the magnetic field. Temperature was varied from +25°C to -30°C. At temperatures lower than -30°C peak broadening became so great as to severely limit the utility of the spectra.

The ^{31}P spectra were recorded on adducts contained in sealed tubes at 24.29 MHz. Phosphorus oxychloride, $POCl_3$, in small capillary tubes was used as external standard. The 300 p.p.m. scale was calibrated by comparing J_{PH} values against the J_{PH} values of the same compound obtained from ^{1}H n.m.r. Additional calibration of the 300 p.p.m. scale was effected in its use during the ^{19}F investigation. CH_3I was the solvent for all systems and the same method of capillary removal was employed as in the ^{11}B study. Temperatures were varied from +25°C to -20°C.

All ^{19}F spectra of the various BF_3 adducts were recorded on solution samples in sealed tubes at 56.45 MHz. Fluorotrichloromethane, CCl_3F, was used as internal reference, with scale setting at 300 p.p.m. Calibration was effected using a mixture of CCl_3F and trifluoroacetic acid-d_1 (TFA) by checking the correspondence between the 9 x 10 p.p.m. scale and the 300 p.p.m. scale. CH_2Cl_2 was employed as solvent because of the greater solubility of the BF_3 complexes. This permitted recording the spectra from +25°C to as low as -90°C.

2. Raman Spectra. Raman spectra were recorded on solid samples in thin-walled glass tubes similar to Type E with a constriction for torch sealing located about 5 cm from the bottom. A Spectra-Physics Model 700 Raman Spectrophotometer was used in conjunction with a Model 164 Argon-ion laser and a Model 265 Exciter Unit. A typical power output was varied between 100 and 300 milliwatts; the 20492 cm^{-1} line was employed as the exciting frequency. Prior to use the instrument was corrected

to zero wave numbers and checked against the spectrum of CCl_4[9] for precision and polarization efficiency.

Polarization data was secured using CH_3I and CH_2Cl_2 solution of the adducts in capped solution cells. The low solubility of the adducts required high instrument gains and laser output between 300 and 700 mw. Slit apertures, scan rates and scale settings were varied as conditions required.

3. Infrared Spectra. The infrared spectra were obtained on a Beckman IR 12 spectrophotometer from 200 cm^{-1} to 4000 cm^{-1}. CsI pellets and Nujol mulls between CsI plates were used for solid samples. Typical KBr solution cells were used for CH_3I and CH_2Cl_2 solution spectra. The spectrometer calibration was periodically checked against the 3027.1 cm^{-1}, 1601.4 cm^{-1}, and 1028.0 cm^{-1} bands of the polystyrene spectrum.

Spectra of gaseous samples were recorded in typical gas sample cells, 10 cm in length with KBr plates.

C. PREPARATIONS

1. Phosphine-d_3, PD_3. Phosphorus trichloride (Anachemia, Toronto) was reduced with lithium aluminum deuteride following the method of Schlesinger and co-workers:[10]

$$3\ LiAlD_4 + 4\ PCl_3 \xrightarrow[25^oC]{diglyme} 4\ PD_3 + 3\ AlCl_3 + 3\ LiCl.$$

The reaction was carried out in a 250 ml reaction vessel (A) equipped with stirring bar and dropping funnel. After evacuating the system, 2.0 cc PCl_3 in 10 ml of dry diglyme (diethyleneglycol methyl ether) was allowed to drip slowly on to a vigorously stirred slurry of 1 g $LiAlD_4$

(Alpha Inorganics, Beverly, Mass.) in 50 ml of dry diglyme. Every half minute the vessel was opened to the trap system at -196°C until all but a small quantity of PCl_3 solution had been added. Distillation of the product through a trap at -126°C yielded pure PD_3 in the -196°C trap. Its infrared spectrum was identical with the reported spectrum.[11] Yields were between 60 - 70%. PD_3 was stored at room temperature in vessel G with greased tap.

2. Methylphosphine and Methyl-d_3-phosphine, CH_3PH_2 and CD_3PH_2. Employing a modified procedure of Jolly,[12] potassium hydroxide powder (60 g, Fisher, AR, Toronto) was placed in reaction vessel (A) equipped with an efficient stirring mechanism and a dropping funnel. Eighty ml dimethyl sulfoxide was added to make a slurry. All joints were greased with Dow Corning silicone grease. The system was thoroughly evacuated and the flask isolated from the line. Pure phosphine (Matheson, Whitby, Ont.) was admitted to the line in a measured quantity and then allowed to react with the KOH slurry. Consumption of PH_3 was followed by observing the manometer and by the growing intensity of the yellow coloration that accompanies the formation of the PH_2^- ion. When the first portion of PH_3 had been comsumed the flask was again isolated, another measured amount of gas was admitted to the line and the procedure repeated until 24 mmole of PH_3 had reacted. A solution of 4 ml CH_3I and 20 ml DMSO was added to the dropping funnel and the system was again evacuated. The flask was closed, about 1 ml of the solution was added. After 1 minute the flask was opened to a trap system at -78°C and -196°C. The process was repeated until all but a small quantity of

solution had been added from the dropping funnel. Decoloration marks the end point of the reaction, but it is best to stop just a bit before the system goes completely colorless. In this way it is possible to avoid contaminating the product with unreacted methyl iodide. The contents of the -196°C trap were repeatedly distilled through a system at -96°C, -126°C, and -196°C. The -126°C product was retained.

For methyl-d_3-phosphine, CD_3I (Stohler Isotope Chemicals, Montreal, 1% ^1H impurity) was used in the second step.

The purity of methylphosphine was checked by infrared[13] and by n.m.r. analysis.[14,15] The n.m.r. spectrum of CD_3PH_2 indicated ca. 4% methyl proton impurity. A yield of 75% was typical. The gases were stored at -196°C in vessel (G) with greased taps.

3. Dimethylphosphine and dimethyl-d_6-phosphine, $(CH_3)_2PH$ and $(CD_3)_2PH$.

A preparation analogous to that used for the monosubstituted phosphine was employed.[16] The original charge of CH_3I solution was added to the closed system rapidly (within the space of one minute) except for a small amount which must be retained in the dropping funnel. (Decoloration should ensue; the flask may be opened to the line if a positive pressure build-up is feared. An auxiliary manometer directly connected to the flask is recommended so that pressure increments can be readily monitored without opening the flask to the line.) The newly formed methylphosphine was allowed to remain in contact with the KOH-DMSO slurry for 1 - 2 hours with constant stirring. The second deprotonation was accompanied by the appearance of the blue-green $MePH^-$ ion. When most of the gas had reacted the system was evacuated and a second charge of CH_3I solution was added in the step-wise manner of the previous preparation. The contents of the -196°C trap were distilled through a system at -96°C, -126°C, and -196°C. That of the -96°C trap was retained. The dimethylphosphine was kept at 0°C in the trap for 1 hour to permit the conversion of any CH_3I into the the non-volatile, Me_3PHI.[16] The purity of the compounds was checked against the published infrared[17] and n.m.r. spectra.[14,15] The n.m.r. spectrum of $(CD_3)_2PH$ indicated a low degree of methyl-proton impurity. Yields were generally low; between 25 - 35% based on PH_3. The gases were stored in vessel (G) with greased taps.

4. Hydrogen Iodide, HI. Although HI may be obtained by pumping on hydriodic acid, it can be quickly and efficiently prepared by the method outline by Vogel.[18] A 250 ml (A) reaction vessel with stirring bar and fitted with a dropping funnel was charged with 10 g of red phosphorus (Fisher). The adapter to the vacuum line was plugged with glass wool to reduce contamination of the line by iodine vapor. The system was evacuated and a solution consisting of 4 g iodine and 8 g hydriodic acid (ca. 5 ml, Anachemia) was added dropwise. The reaction occurred at room temperature and HI was collected in a pure state at -196°C after first passing through traps at -23°C and -78°C.

5. Diborane, B_2H_5. In a modified procedure of Weiss and Shapiro,[19] 2.5 g of solid potassium borohydride (Alpha Inorganics) was slowly added to 175 ml of 96% H_2SO_4. A reaction vessel (A), fitted with tipping tube and efficient stirring mechanism was used. The adapter leading to the

vacuum line was plugged with glass wool to prevent undue contamination of the line with polymeric boron hydrides. After thorough evacuation and with the system open to the traps, diborane was collected at -196°C and impurities retained at -78°C. The hydrogen simultaneously produced was monitored and periodically pumped off through the trap system. Reaction temperatures near 0°C favored higher yields. The product was purified by collecting the contents of all three -196°C traps and distilling the material through a trap at -126°C. The product was checked for purity by infrared spectroscopy.[20] Yields varied between 40 and 50% depending on the dryness of the H_2SO_4. Diborane was stored in vessel (G) with greased taps.

6. Monobromodiborane, B_2H_5Br. In a modification of previous procedures diborane and boron tribromide were mixed in reaction vessel (B) in a ratio of 5:2 and set at 0°C for three hours.[21,22] The contents were then passed through traps at -78°C, -126°C, and -196°C. B_2H_5Br was retained in the -126°C trap while the contents of the other two were returned to the reaction vessel. The process was repeated several times until nearly total conversion had been realized.

$$5\ B_2H_6 + 2\ BBr_3 \xrightarrow{0^\circ C} 6\ B_2H_5Br$$

The crude material was separated from traces of dibromoborane, $BHBr_2$, by repeated distillation through a trap at -96°C. The infrared spectrum[23] as well as the ^1H and ^{11}B spectra[24] were used to ascertain purity. The product was kept at -196°C in storage vessel (B). Yields of 80% were typical.

7. Monoiododiborane, B_2H_5I. Diborane and hydrogen iodide[25,26] were distilled into reaction vessel (B) at -196°C in a 7:5 ratio. After 10 hours at 0°C the progress of the reaction was monitored in terms of the amount of hydrogen present at -196°C. The reaction was periodically monitored over a space of 3 days, with the H_2 being removed each time, until a nearly stoichiometric quantity of H_2 had been produced according to the equation:

$$B_2H_6 + HI \xrightarrow{0^oC} B_2H_5I + H_2$$

Initially the reaction was accompanied by extensive discoloration, probably due to the formation of elemental iodine. With passage of time the contents went nearly colorless. Distillation through traps at 0°C, -78°C, and -196°C yielded B_2H_5I at -78°C. Other materials were discarded. The infrared spectrum of the compound corresponded with that previously published.[26] Yields ran between 40 and 50% based on HI. B_2H_5I was retained at -196°C in storage vessel (B).

D. COMMERCIALLY OBTAINED STARTING MATERIALS.

1. Phosphine, PH_3. Commercially produced phosphine (Matheson) was purified before use by distillation through a trap at -126°C. Its infrared spectrum[27] was identical with that of the pure material. It was stored at room temperature in vessel (G) with greased tap.

2. Phenylphosphine, $C_6H_5PH_2$. Commercially obtained phenylphosphine, $PhPH_2$, (Research Organics/Inorganics, Hillside, N. J.) was used without further purification. It was stored in a corked 25 ml erlenmeyer flask which, in turn, was placed in a wide-mouth specimen bottle with plastic

cap. The material was stored under refrigeration. It is flammable in air and has a very offensive odor. It must always be handled in a nitrogen-filled dry-box.

3. Diphenylphosphine, $(C_6H_5)_2PH$. Ph_2PH was obtained from the same source as phenylphosphine; it was stored and handled in similar fashion.

4. Hydrogen Chloride, HCl. Commercial hydrogen chloride from small lecture bottles (Matheson) was transferred directly into storage vessel (G) via the vacuum line. HCl (g) can also be very conveniently obtained by pumping on concentrated hydrochloric acid in vessel (A) attached to the vacuum line. Pumping through a trap system of -76°C and three -196°C units yields a large quantity of pure HCl in a short time.

5. Hydrogen Bromide, HBr. Commercial hydrogen bromide (Matheson) was transferred in the vacuum line through a trap at -126°C into a storage vessel (G) with greased stopcock.

6. Boron Trifluoride, BF_3. The commercial product (Matheson) was stored at room temperature in vessel (G) with greaseless tap. When necessary, the gas was distilled through a trap at -96°C.[28] The infrared spectrum of the material which collected at -196°C checked with that of the pure material.[29]

7. Boron Trichloride, BCl_3. Commercial BCl_3 (Matheson) was distilled on the vacuum line at -78°C, -112°C, and -196°C. The -112°C fraction was retained and stored in vessel (B) with greaseless tap. When necessary the material was redistilled prior to use.[30] The infrared spectrum was

identical to that of the pure material.[31]

8. Boron Tribromide, BBr_3. Boron tribromide (Alpha Inorganics) was distilled through traps at -45°C, -78°C, and -196°C. The -78°C fraction was retained and stored in Vessel (B). Redistillation was carried out when required. The infrared spectrum was checked against that of the pure material.[32]

9. Boron Triiodide, BI_3. The commercially obtained, white, crystalline compound (Alpha Inorganics) was stored in small capped vials under refrigeration. Prior to use, the requisite amount of BI_3 was transferred to a small vial under moisture-free conditions. Benzene and a trace of elemental mercury were added. Agitation of the BI_3 solution with Hg removed whatever free iodine was present. The solution was decanted and used immediately. No further purity checks were made.

SOLVENTS.

1. Methyl Iodide, CH_3I. Although methyl iodide was used in certain methylation procedures, its main function in this research was as solvent for the adduct systems. Analytical grade CH_3I (Fisher) was transferred to small (B) storage vessels and was distilled from them on the vacuum line when needed. A small piece of elemental copper was placed in the vessel to inhibit decomposition and the solvent was generally stored in darkness when not in use. Raman, infrared, and n.m.r. spectra were run on liquid samples. These were used for reference purposes during the investigation.

2. Methyl-d_3-Iodide, CD_3I. Aside from certain methylation reactions, this material served mainly as solvent in the ^1H n.m.r. study of the PH_3BX_3 and $MePH_2BX_3$ series. The n.m.r. peak height attributable to the <1% ^1H impurity (Stohler) aided in estimating the extent of adduct solubility. It was handled in the same fashion as described for CH_3I.

3. Methylene Chloride, CH_2Cl_2. Spectrometric grade methylene chloride (J. T. Baker, Phillipsburg, N. J.) was used as obtained and stored in vessel (B). When not in use it was stored in the dark. Raman, infrared, and n.m.r. spectra were recorded for reference purposes.

4. Benzene, C_6H_6. Reagent grade benzene (Aldrich, Milwaukee, Wis.) was used as solvent for the BI_3 system. It was taken as required from the original container.

5. Dimethylsulfoxide, $(CH_3)_2SO$. Reagent grade DMSO was used as obtained from the commercial supplier (Fisher).

6. Diethylene Glycol Methyl Ether, $CH_3O(CH_2)_2O(CH_2)_2OCH_3$. Diglyme, reagent grade (Fisher) was stored over sodium prior to use and was decanted when needed.

SECTION 2

^{1}H NUCLEAR MAGNETIC RESONANCE DATA

A. THE TEMPERATURE DEPENDENT STUDY

1. The Phosphine-Boron Trihalide Adducts.
2. The Methylphosphine-Boron Trihalide Adducts.
3. The Dimethylphosphine-Boron Trihalide Adducts.
4. The Phenylphosphine-Boron Trihalide Adducts.
5. The Diphenylphosphine-Boron Trihalide Adducts.

TABLE 2A - 1

The ^1H n.m.r. parameters (δ in p.p.m. ± 0.05 p.p.m. relative to internal TMS; J_{PH} in Hz ± 2 Hz) for the adduct series PH_3BX_3 (X = H, Cl, Br, I)* recorded in CD_3I as a function of temperature.

	PH_3BH_3		PH_3BCl_3		PH_3BBr_3		PH_3BI_3	
	δ	J_{PH}	δ	J_{PH}	δ	J_{PH}	δ	J_{PH}
-70°C	-4.52	368	-5.92	426	-6.44	429	-7.40	432
-50	-4.49	366	-5.90	424	-6.44	429	-7.40	432
-40	-4.50	370	~-5.6	~412	-6.40	428	-7.40	430
-20	-4.29	370	~-5.4	~400	-6.34	428	-7.40	430
-10	-4.29	370	~-5.4	~400	-6.30	427	-7.40	430
0	-4.26	370	~-5.4	~400	-6.27	426	-7.35	430
+25	†		-5.37	396	-6.20	424	-7.26	428

*The adduct PH_3BF_3 did not form at the temperatures specified.

†Bubbling of the adduct was taken as a sign of rapid decomposition and the operation was terminated.

TABLE 2A - 2

The ^1H n.m.r. parameters (δ in p.p.m. ± 0.05 p.p.m. relative to internal TMS; J_{PH} in Hz ± 2 Hz) for the adduct series $CD_3PH_2BX_3$ (X = H, F, Cl, Br, I) recorded in CD_3I as a function of temperature.

	$CD_3PH_2BH_3$		$CD_3PH_2BF_3$		$CD_3PH_2BCl_3$		$CD_3PH_2BBr_3$		$CD_3PH_2BI_3$	
	δ	J_{PH}	δ	J_{PH}	δ	J_{PH}	δ	J_{PH}	δ	J_{PH}
-70°C	-4.62	372	-4.28	355	-5.30	428	-5.60	430	-6.20	434
-50	-4.62	372	-4.28	350	-5.30	426	-5.60	430	-6.20	434
-40	-4.62	372	-4.26	350	-5.26	422	-5.60	428	-6.20	434
-20	-4.60	370	-4.22	346	-5.26	420	-5.58	428	-6.20	434
-10	-4.60	370	-4.15	332	-5.24	418	-5.58	428	-6.20	434
0	-4.56	365	-3.92	315	-5.20	416	-5.58	428	-6.20	434
+25	-4.52	362	-3.72	301	-5.14	416	-5.54	426	-6.18	434

TABLE 2A - 3

The ^1H n.m.r. parameters (δ in p.p.m. ± 0.05 p.p.m. relative to internal TMS; J_{PH} in Hz ± 2 Hz) for the adduct series $(CD_3)_2PHBX_3$ (X = H, F, Cl, Br, I) recorded in CD_3I as a function of temperature.

	$(CD_3)_2PHBH_2$		$(CD_3)_2PHBF_3$		$(CD_3)_2PHBCl_3$		$(CD_3)_2PHBBr_3$		$(CD_3)_2PHBI_3$	
	δ	J_{PH}	δ	J_{PH}	δ	J_{PH}	δ	J_{PH}	δ	J_{PH}
-70°C	-4.78	369	-4.80	384	-5.14	420	-5.40	429	-5.45	432
-60			-4.80	384	-5.14	420	-5.40	429	-5.45	432
-50			-4.80	381	-5.14	417	-5.40	426	-5.50	432
-40	-4.78	369	-4.80	381	-5.14	417	-5.42	426	-5.46	432
-30			-4.80	381	-5.10	417	-5.40	426	-5.46	429
-20			-4.80	378	-5.10	414	-5.36	426	-5.46	429
-10	-4.78	365	-4.76	378	-5.06	414	-5.36	426	-5.42	429
0	-4.78	369	-4.72	378	-5.10	414	-5.36	423	-5.42	429
+25	-4.78	367	-4.66	375	-5.10	414	-5.28	423	-5.40	429
+35			-4.66	372	-5.10	414	-5.28	423	-5.38	429
+45			-4.66	372	-5.12	414	-5.28	423	-5.38	429
+55			-4.66	369	-5.12	414	-5.28	420	-5.34	429
+65			-4.54	354	-5.12	414	-5.32	420	-5.38	429
+75			-4.50	351	-5.12	414	-5.32	420	-5.40	429

TABLE 2A - 4

The ^1H n.m.r. parameters (δ in p.p.m. ± 0.05 p.p.m. relative to internal TMS; J_{PH} in Hz ± 2 Hz) for the adduct series $PhPH_2BX_3$ (X = H, F, Cl, Br, I) recorded in CD_3I as a function of temperature.

	$PhPH_2BH_3$		$PhPH_2BF_3$		$PhPH_2BCl_3$		$PhPH_2BBr_3$		$PhPH_2BI_3$	
	δ	J_{PH}	δ	J_{PH}	δ	J_{PH}	δ	J_{PH}	δ	J_{PH}
-70°C	-5.65	375	-4.96	284	-6.44	420	-6.82	430	-7.44	434
-60	-5.65	375	-4.92	284						
-50	-5.60	375	-4.90	284						
-40	-5.60	375	-4.86	288	-6.42	420	-6.78	430	-7.40	432
-30	-5.60	375	-4.70	266						
-20	-5.60	373	-4.50	254	-6.42	420	-6.76	430	-7.40	432
0	-5.58	372	loss of signal						-7.40	430
+25	-5.58	372			-6.28	418	-6.66	428	-7.32	430
+35	-5.58	369			-6.24	418	-6.62	428	-7.30	430
+45	-5.58	370			-6.22	418	-6.62	428	-7.30	430
+55	-5.60	370			-6.22	418	-6.66	430	-7.30	428
+65	-5.60	370			-6.20	416	-6.66	430	-7.30	428
+75	-5.60	372			-6.20	416	-6.62	424	-7.28	428

TABLE 2A - 5

The ^1H n.m.r. parameters (δ in p.p.m. ± 0.05 p.p.m. relative to internal TMS; J_{PH} in Hz ± 2 Hz) for the adduct series Ph_2PHBX_3 (X = H, F, Cl. Br, I) recorded in CD_3I as a function of temperature.

	Ph_2PHBH_3		Ph_2PHBF_3		Ph_2PHBCl_{33}		Ph_2PHBBr_3		Ph_2PHBI_3	
	δ	J_{PH}	δ	J_{PH}	δ	J_{PH}	δ	J_{PH}	δ	J_{PH}
-70°C	-6.40	381	*		-6.80	422	-7.00	435	-7.59	441
-60	-6.40	381	-6.48	389					-7.59	441
-50	-6.40	381	-6.46	387						
-40	-6.40	381	-6.40	385	-6.80	420	-7.00	432	-7.59	441
-30	-6.40	380	-6.46	384						
-20	-6.40	380	-6.50	386	-6.76	420	-6.92	432	-7.44	438
-10	-6.36	379	-6.66	394			-6.92	432	-7.42	435
0	-6.36	379	-6.70	396	-6.70	417	-6.92	431	-7.36	435
+25	-6.36	378	-6.90	399	-6.68	417	-6.88	429	-7.36	435
+35	-6.36	378	loss of signal		-6.60	416	-6.90	427	-7.36	435
+45	-6.36	378			-6.62	415	-6.86	427	-7.36	435
+55	-6.40	378			-6.62	415	-6.88	427	-7.36	435
+65	-6.40	378			-6.66	415	-6.84	429	-7.38	438
+75	-6.40	378			-6.64	415	-6.84	426	-7.38	438

*signal lost as a result of solution freeze-up.

B. APPLICATION OF THE COULSON RELATIONSHIP, $1 + \lambda^2 \cos\theta = 0$.

1. The Tetrahedral HCH Angle.

$$\cos 109^\circ 52' = -0.3405$$

$$\lambda^2 = \frac{-1}{-0.3405} = 3 \text{ (p-contribution)}$$

$$3/4 = 75\% \text{ p-character}$$

$$1/4 = 25\% \text{ s-character}$$

2. The HPH Angle in $MePH_2$.

$$\theta = 93.4^\circ$$

$$\cos 93.4^\circ = -0.0593$$

$$\lambda^2 = \frac{-1}{-0.0593} = 16.8$$

$$1/17.8 = 5.5\% \text{ s-character}$$

3. The HPH Angle in $MePH_2BH_3$.

$$\theta = 99.9^\circ$$

$$\cos 99.9^\circ = -0.1719$$

$$\lambda^2 = \frac{-1}{-0.1719} = 5.82$$

$$1/6.82 = 14.7\% \text{ s-character}$$

SECTION 3

HALOGEN REDISTRIBUTION

A. THE ^{1}H N.M.R. PARAMETERS OF THE MIXED SYSTEMS.

B. THE EQUILIBRIUM STUDY -- INTEGRATION DATA.

TABLE 3A

The ^{1}H n.m.r. parameters (δ in p.p.m. ± 0.05 p.p.m. relative to internal TMS; J_{PH} in Hz ± 2 Hz) for the adduct series $(CD_3)_nPH_{3-n}BX_2Y$ ($n = 0, 1$; $X \neq Y = F, Cl, Br, I$) recorded in CD_3I at -70°C.

ADDUCT	δ	J_{PH}	ADDUCT	δ	J_{PH}
PH_3BCl_3	-5.82	416	$CD_3PH_2BCl_3$	-5.28	422
PH_3BCl_2Br	-6.00	424	$CD_3PH_2BCl_2Br$	-5.40	426
PH_3BClBr_2	-6.28	426	$CD_3PH_2BClBr_2$	-5.50	426
PH_3BBr_3	-6.42	428	$CD_3PH_2BBr_3$	-5.62	432
PH_3BCl_3	-5.94	420	$CD_3PH_2BCl_3$	-5.32	420
PH_3BCl_2I	-6.42	428	$CD_3PH_2BCl_2I$	-5.62	424
PH_3BClI_2	-6.94	430	$CD_3PH_2BClI_2$	-5.88	430
PH_3BI_3	-7.42	436	$CD_3PH_2BI_3$	-6.22	434
PH_3BBr_3	-6.44	428	$CD_3PH_2BBr_3$	-5.68	428
PH_3BBr_2I	-6.74	432	$CD_3PH_2BBr_2I$	-5.80	430
PH_3BBrI_2	-7.08	434	$CD_3PH_2BBrI_2$	-5.96	432
PH_3BI_3	-7.40	436	$CD_3PH_2BI_3$	-6.20	430
PH_3BBr_3	-6.48	428	$CD_3PH_2BBr_3$	-5.62	430
PH_3BBr_2F	-6.00	410	$CD_3PH_2BBr_2F$	-5.30	422
PH_3BBrF_2	-5.88	404	$CD_3PH_2BBrF_2$	-4.98	406
			$CD_3PH_2BF_3$	-4.60	384

TABLE 3B - 1

Equilibrium constants for redistributions (1) and (2) as calculated in terms of mole percent* for various molar ratios of PH_3BCl_3 and PH_3BI_3.

RATIOS PH_3BCl_3:PH_3BI_3	$[PH_3BCl_3]$	$[PH_3BCl_2I]$	$[PH_3BClI_2]$	$[PH_3BI_3]$	K_1	K_2
1.0 : 0.8	46.49 (86)	12.97 (24)	3.78 (7)	36.76 (68)	0.299	0.093
1.0 : 1.0	30.77 (40)	13.85 (18)	7.69 (10)	47.69 (62)	0.389	0.187
1.0 : 1.2	32.45 (49)	21.85 (33)	3.98 (6)	41.72 (63)	0.619	0.104
1.0 : 1.4	29.95 (56)	20.86 (39)	10.70 (20)	38.50 (72)	0.641	0.302
1.0 : 1.6	22.22 (50)	14.22 (32)	6.67 (15)	56.89 (128)	0.470	0.160
1.6 : 1.0	23.16 (44)	16.32 (31)	7.37 (14)	53.15 (101)	0.510	0.183
1.4 : 1.0	31.82 (56)	15.91 (28)	6.82 (12)	45.45 (80)	0.434	0.169
1.2 : 1.0	40.88 (65)	15.09 (24)	6.92 (11)	37.11 (59)	0.381	0.181
0.8 : 1.0	34.87 (53)	17.76 (27)	7.90 (12)	39.47 (60)	0.489	0.209
0.8 : 1.2	31.38 (59)	15.43 (29)	5.85 (11)	47.34 (89)	0.429	0.148
1.2 : 0.8	28.28 (56)	17.17 (34)	5.06 (10)	49.49 (98)	0.502	0.123

*Values in parentheses are heights of integration lines.

TABLE 3B - 2

Equilibrium constants for redistributions (1) and (2) as calculated in terms of mole percent* for various molar ratios of PH_3BBr_3 and PH_3BI_3.

RATIOS $PH_3BBr_3:PH_3BI_3$	$[PH_3BBr_3]$	$[PH_3BBr_2I]$	$[PH_3BBrI_2]$	$[PH_3BI_3]$	K_1	K_2
0.8 : 1.0	20.69 (36)	34.48 (60)	31.61 (55)	13.22 (23)	1.93	2.06
1.0 : 1.0	15.52 (27)	29.89 (52)	34.48 (60)	20.11 (35)	1.76	1.87
1.2 : 1.0	19.88 (32)	34.16 (55)	31.68 (61)	14.28 (23)	1.92	1.99
1.4 : 1.0	15.79 (27)	30.41 (52)	33.92 (58)	19.88 (34)	1.78	1.84
1.6 : 1.0	17.68 (38)	34.42 (74)	34.88 (75)	13.20 (28)	2.16	2.42
1.0 : 1.6	11.57 (14)	29.75 (36)	37.19 (45)	21.49 (26)	2.07	2.12
1.0 : 1.4	14.58 (21)	31.25 (45)	29.17 (42)	25.00 (36)	1.79	1.40
1.0 : 1.2	18.56 (31)	32.93 (55)	31.14 (52)	17.37 (24)	1.81	1.82
1.0 : 0.8	14.63 (24)	29.27 (48)	35.98 (59)	20.12 (33)	1.80	1.99
1.2 : 0.8	22.28 (41)	34.24 (63)	30.44 (56)	13.04 (24)	1.85	1.95
0.8 : 1.2	15.38 (20)	29.23 (38)	35.39 (46)	20.00 (26)	1.74	1.93

*Values in parentheses are heights of integration lines.

TABLE 3B - 3

Equilibrium constants for redistributions (1) and (2) as calculated in terms of mole percent* for various molar ratios of PH_3BCl_3 and PH_3BBr_3.

RATIOS PH_3BCl_3:PH_3BBr_3	$[PH_3BCl_3]$	$[PH_3BCl_2Br]$	$[PH_3BClBr_2]$	$[PH_3BBr_3]$	K_1	K_2
1.0 : 0.8	7.38 (9)	25.41 (31)	44.26 (54)	22.95 (28)	2.36	2.81
1.0 : 1.0	15.18 (17)	37.50 (42)	34.82 (39)	12.50 (14)	2.65	2.61
1.0 : 1.2	13.85 (18)	38.46 (50)	35.38 (43)	12.31 (16)	2.89	2.76
1.0 : 1.4	11.36 (20)	32.96 (58)	37.50 (66)	18.18 (32)	2.45	2.35
1.0 : 1.6	too heavy in BBr_3; BCl_3 peak unobserved					
1.6 : 1.0	24.14 (35)	39.31 (57)	28.27 (41)	8.28 (12)	2.32	2.39
1.4 : 1.0	14.29 (20)	36.43 (51)	35.71 (50)	13.57 (19)	2.59	2.58
1.2 : 1.0	15.79 (24)	36.19 (55)	33.55 (51)	14.47 (22)	2.36	2.25
0.8 : 1.0	9.00 (10)	25.24 (28)	38.74 (43)	27.02 (30)	2.04	2.12
0.8 : 1.2	7.70 (10)	26.15 (34)	40.00 (52)	26.15 (34)	2.26	2.30
1.2 : 0.8	24.34 (37)	40.79 (62)	27.63 (42)	7.24 (11)	2.51	2.55

*Values in parentheses are heights of integration lines.

SECTION 4

MONOIODODIBORANE

In the course of this investigation it became necessary to synthesize the monoiodo derivative of diborane, B_2H_5I. Although the compound has long been known, having first been reported by Stock and Pohland,[25] it has only been partially characterized to date. In the original report a melting point of $-110^{\circ}C$ and a vapor pressure of 8 cm Hg at $0^{\circ}C$ were given. The compound was used as a starting material in a Wurtz-type synthesis with elemental sodium to yield B_4H_{10}.

In addition to the original method of preparation, which was that followed in this investigation (APPENDIX, Section 1C, 7) other synthetic routes have been reported.[26,33] In one of these[26] the infrared spectrum of the gaseous compound is reproduced and discussed by way of comparison with those of B_2H_5Br and B_2H_5Cl.[23] The frequency listings are not given nor are explicit assignments made.

Although substantial Raman work has been done on the methyl-substituted diboranes,[34,35] no Raman studies have been reported on any B_2H_5X species (X = Cl, Br, I).

Both ^1H and ^{11}B n.m.r. spectra of monobromodiborane have been published[24] but those of the corresponding iodo-compound have not been reported.

Inasmuch as the preparation of monoiododiborane was required as an initial synthetic step in this investigation and since it had only been partially characterized previously, a more thorough study was made of this compound. Reported below are the results of a molecular weight determination, a vapor pressure study, the ^{1}H and ^{11}B spectral assignments, and the infrared and Raman spectra together with assignments based on analogous systems.*

1. Molecular Weight Determination. Since there had been no previous reports of molecular weight determinations of the compound, it was decided to do this using a method somewhat similar to that described by Shriver.[36] The volume of the molecular weight bulb was initially calibrated using two gases of known molecular weight (PH_3 and GeH_4). A value of 158.4 ± 5 g/mole was obtained for the molecular weight of B_2H_5I. The calculated value is 153.6 g/mole.

2. Vapor Pressure Study. The vapor pressure of the gas was obtained at four different temperatures using a small differential manometer. Since B_2H_5I exhibits some reactivity toward mercury, the material was brought to -130°C and opened to the pump after each vapor pressure determination. In this way any decomposition products formed during the measurement which were volatile at that temperature (e.g., B_2H_6) would be removed. The vapor pressure data are given in Table 4 - 1 in a form suitable for substitution into the modified Clausius-Clapeyron Equation:

$$\log \frac{P_2}{P_1} = \frac{\Delta H_v}{2.303R} \cdot \frac{T_2 - T_1}{T_1 T_2} \quad .$$

---

*A mass spectral investigation was also conducted on an AEI MS 10 instrument for the purpose of further confirmation of assignments. Previous use of the spectrometer had, however, led to contamination by halogens and exchange processes occurring during the work with B_2H_5I produced inconclusive results. The data from this source have therefore been omitted from this report.

TABLE 4 - 1

Vapor pressure data for B_2H_5I

T^oC	T^oK	$\frac{1}{T} \times 10^{-3}$	P (mm Hg)	log P
-74.5	198.7	5.04	2.0	0.301
-44.0	229.2	4.36	14.0	1.146
-25.0	248.2	4.03	29.5	1.470
0.0	273.2	3.66	88.5	1.947

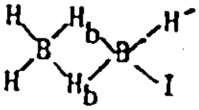
It is to be noted that the vapor pressure at 0^oC is somewhat higher than that previously reported and may indicate the presence of some impurity although a graph of the points yielded a very good straight line fit.

The calculated heat of vaporization, ΔH_v, was found to be 5540 cal/mole and the vapor pressure data for B_2H_5I are summarized by the equation:

$$\log P\ (\text{mm}) = -\frac{1.21 \times 10^3}{T} + 6.390 ,$$

where $1.21 \times 10^3 = \Delta H_v/2.303R$. The boiling point, T_{760}, extrapolated from the above equation is $344.8^oK = 72^oC$. The Trouton Constant, $\Delta H_v/T_{760} = 16.1$ e. u. This value is somewhat lower than normal (ca., 21 e. u.). Low values for the Trouton Constant are generally observed in systems of high volatility.[37] Since the vapor pressure data as well as the calculated boiling point of B_2H_5I are not those of a highly volatile material, it may be that the unstable nature of the compound produced deviations which led to a somewhat low Trouton Constant value.

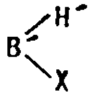
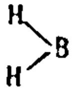
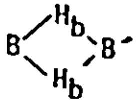
3. The ^{1}H and ^{11}B n.m.r. Spectra. The ^{1}H and ^{11}B parameters for



are recorded in Tables 4 - 2 and 4 - 3, respectively. In each case comparison is made with the analogous B_2H_5Br system. The ^{1}H and ^{11}B n.m.r. spectra are reproduced in Figures 4 - 1 and 4 - 2, respectively.

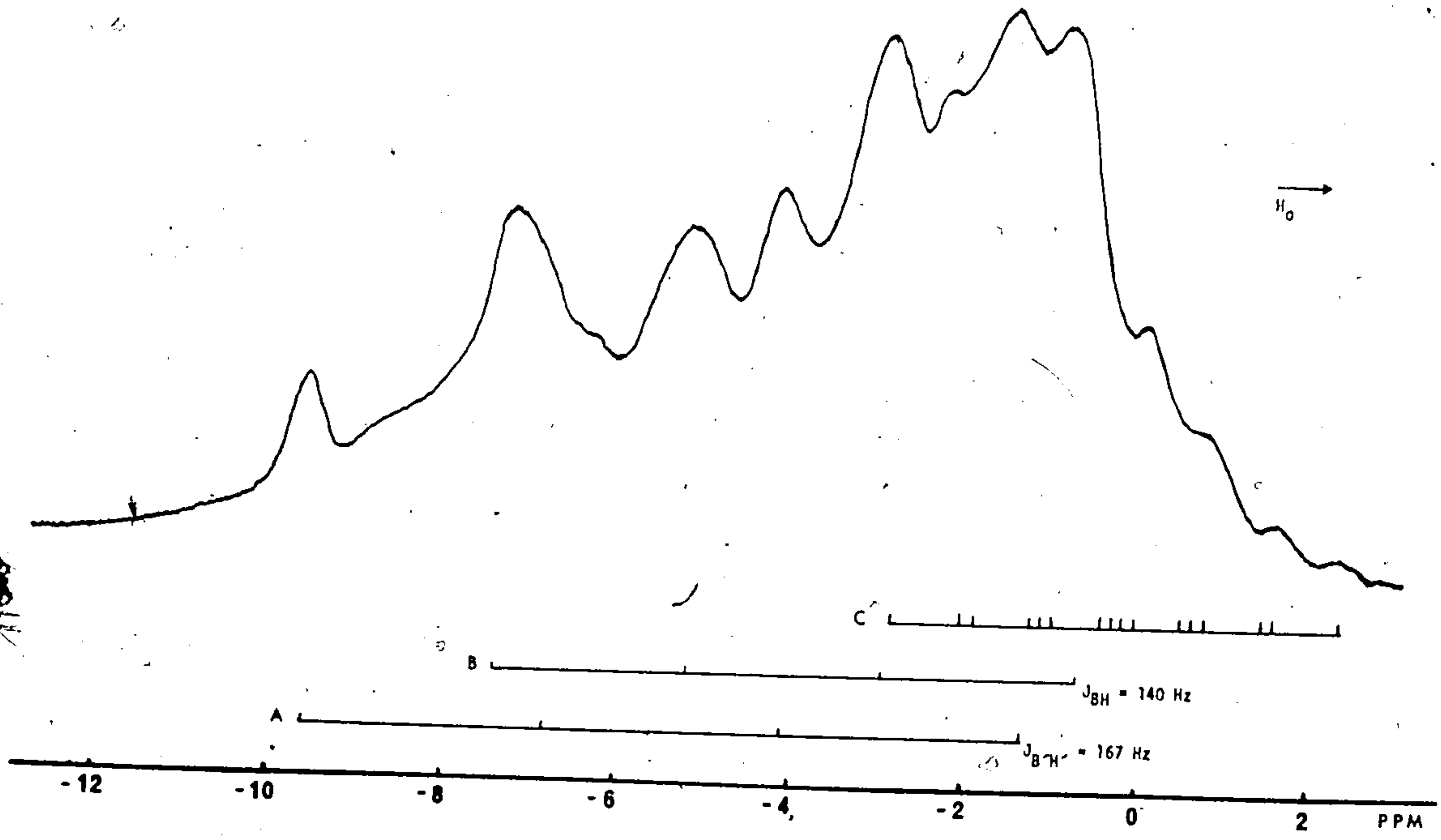
TABLE 4 - 2

The ^{1}H n.m.r. parameters (δ in p.p.m. ± 0.1 p.p.m. relative to external TMS: J_{BH} in Hz ± 5 Hz) for B_2H_5I and $B_2H_5Br^{24}$ at -40°C

	B_2H_5I		B_2H_5Br	
	δ	J_{BH}	δ	J_{BH}
	-5.22	168	-4.98	167
	-4.00	140	-4.02	140
	-0.8 (est.)	-	-1.2 (est)	-

The ^{1}H n.m.r. spectrum is quite similar in pattern and parameter values to those of B_2H_5Br. The resonance of the terminal hydrogen attached to the boron which bears the iodine atom is split into a quartet by boron (I = $^3/_2$), with J_{BH} = 168 Hz. The chemical shift of this multiplet is -5.22 p.p.m. from external TMS. As might be expected, a comparison of the chemical shift values of both halide compounds shows that the resonance of the proton attached to the halide-bearing boron

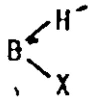
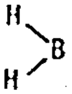
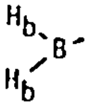
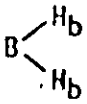
Figure 4 - 1 -- The ^{1}H n.m.r. Spectru of B_2H_5I at -40°C.



atom is most sensitive to substitution. This is good evidence for the correctness of the assignment of the low-field quartet, marked "a", to the resonance of this terminal proton. Additional evidence is provided by comparing relative peak areas of different quartet members, although some difficulty due to overlapping peaks is encountered here. The area under the last peak of the "a" quartet is significantly less than that of any non-overlapping member of the "b" quartet. The "b" series of peaks is assigned to the resonance of the two terminal protons on the other boron atom.

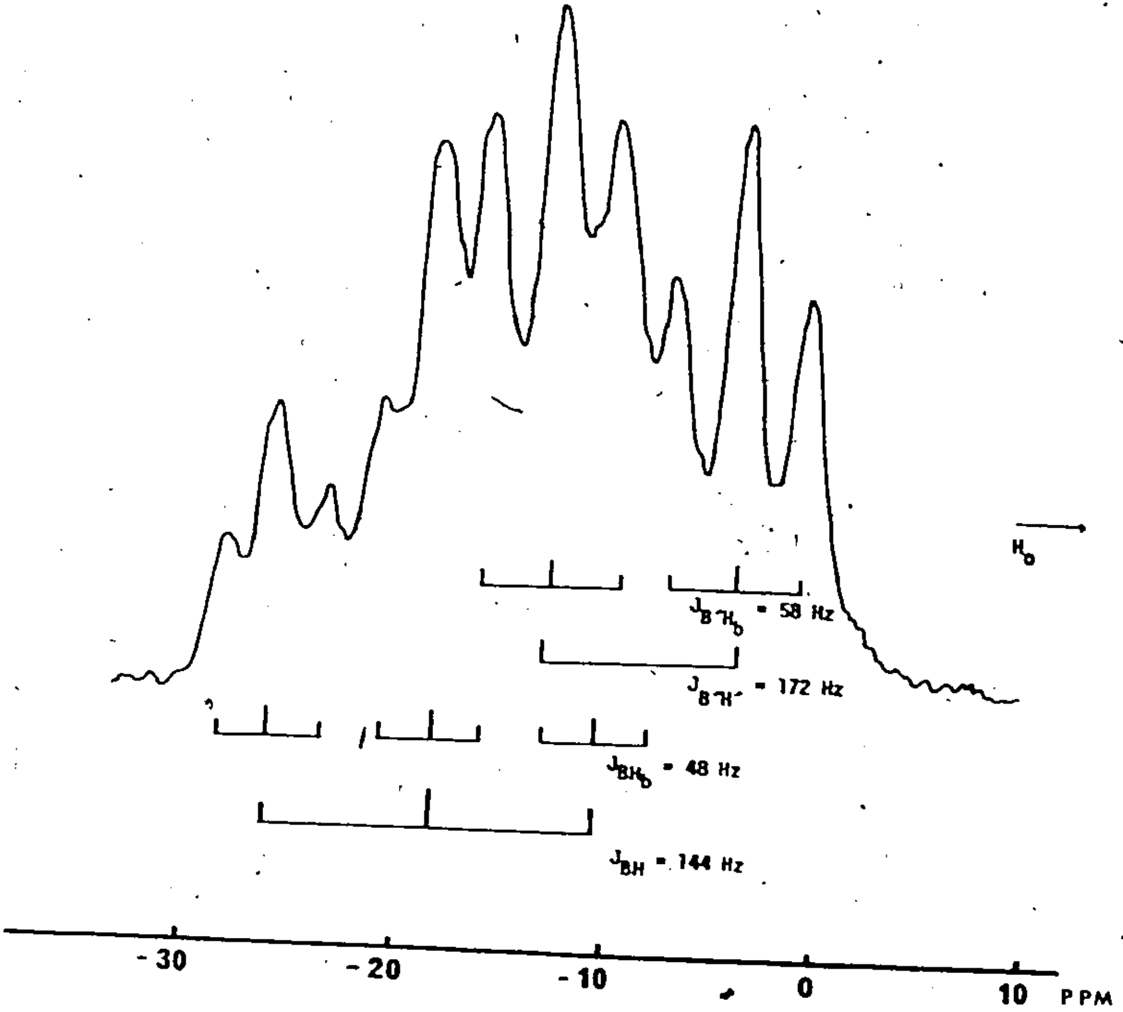
TABLE 4 - 3

The ^{11}B n.m.r. parameters (δ in p.p.m. ± 1 p.p.m. relative to external Et_2OBF_3; J_{BH} in Hz ± 5 Hz) for B_2H_5I and B_2H_5Br[24] at -30°C

	B_2H_5I		B_2H_5Br	
	δ	J_{BH}	δ	J_{BH}
	-7.8	172	-18.9	163
	-18.1	144	-12.2	141
		57.6		56.4
		48.0		44.2

Boron-hydrogen coupling values for the bridging protons could not be assessed from ^{1}H n.m.r. However, a quartet of quartets resulting in a symmetrical arrangement of 16 lines, marked "c", was obtained by

Figure 4 - 2 -- The ^{11}B Spectrum of B_2H_5I at -30°C.



measuring off the J_{BH} values derived from the ^{11}B spectrum. Since the two boron atoms are chemically non-equivalent, each member of the $B'H_b$ quartet ($J_{B'H_b}$ = 56.4 Hz) is split into another quartet, J_{BH_b} = 44.2 Hz, thereby giving rise to the 16 member array.

The ^{11}B n.m.r. spectrum is similar in certain parameter values to that of B_2H_5Br but opposite in pattern. As a result of the ^{11}B investigation of the BX_3 adducts of phosphine and methylphosphine (Chapter IV) it is clear that boron attached to iodine resonates at a position significantly upfield from that of boron attached to bromine. Hence, the reversal of the resonance pattern in B_2H_5I is consistent and is in accord with expectation.

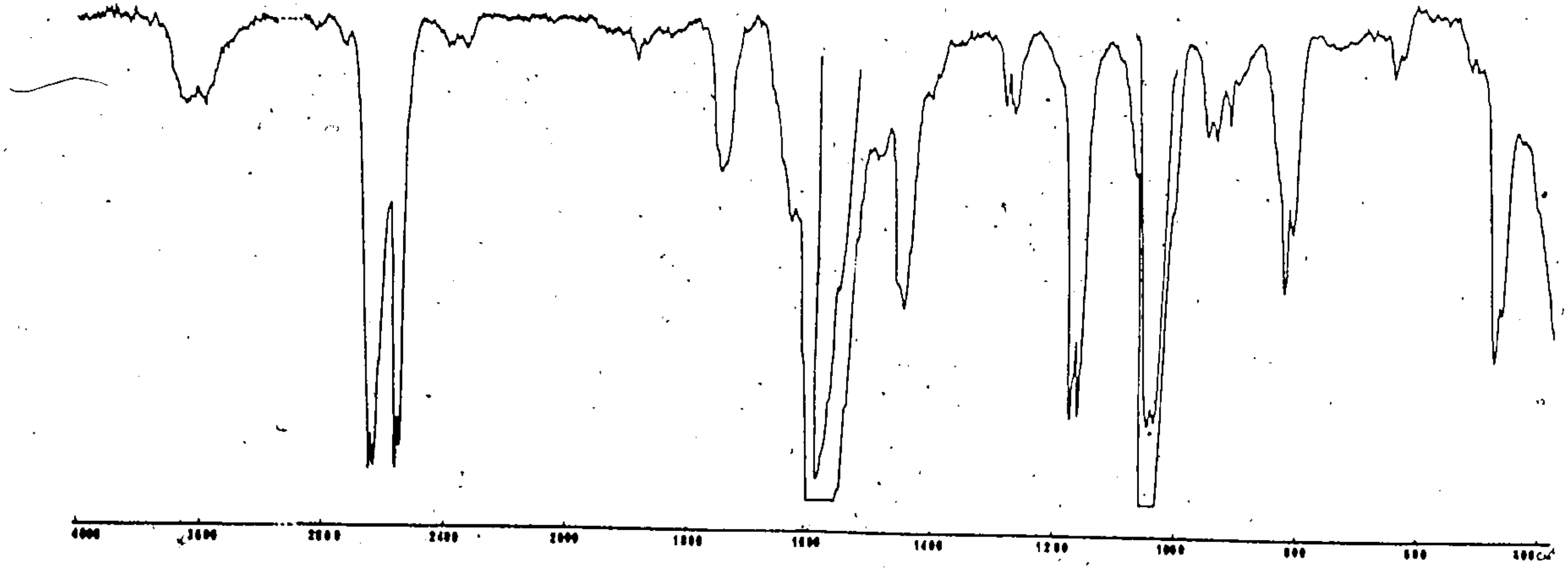
The downfield triplet is assigned to the boron bearing two terminal hydrogens. Each member of this system is further split into 1:2:1 triplets through spin-spin coupling with the two bridged hydrogens. This pattern, apparent in B_2H_5Br is also observed in diborane.[38-41]

The upfield doublet is assigned to the boron attached to iodine, with $J_{B'H'}$ = 172 Hz. Each member of this doublet is further split into 1:2:1 triplets by the bridging hydrogen atoms.

4. <u>The Infrared and Raman Spectra</u>. The infrared spectrum of gaseous B_2H_5I is reproduced in Figure 4 - 3. The Raman spectrum of the neat liquid, displayed in Figure 4 - 4, also shows the spectrum under polarized conditions. All spectra were recorded at ambient temperatures. A correlation of all observed infrared and Raman frequencies is given in Table 4 - 4.

On the basis of infrared[42] and electron diffraction[43] evidence

Figure 4 - 3 -- The Infrared Spectrum of gaseous B_2H_5I.



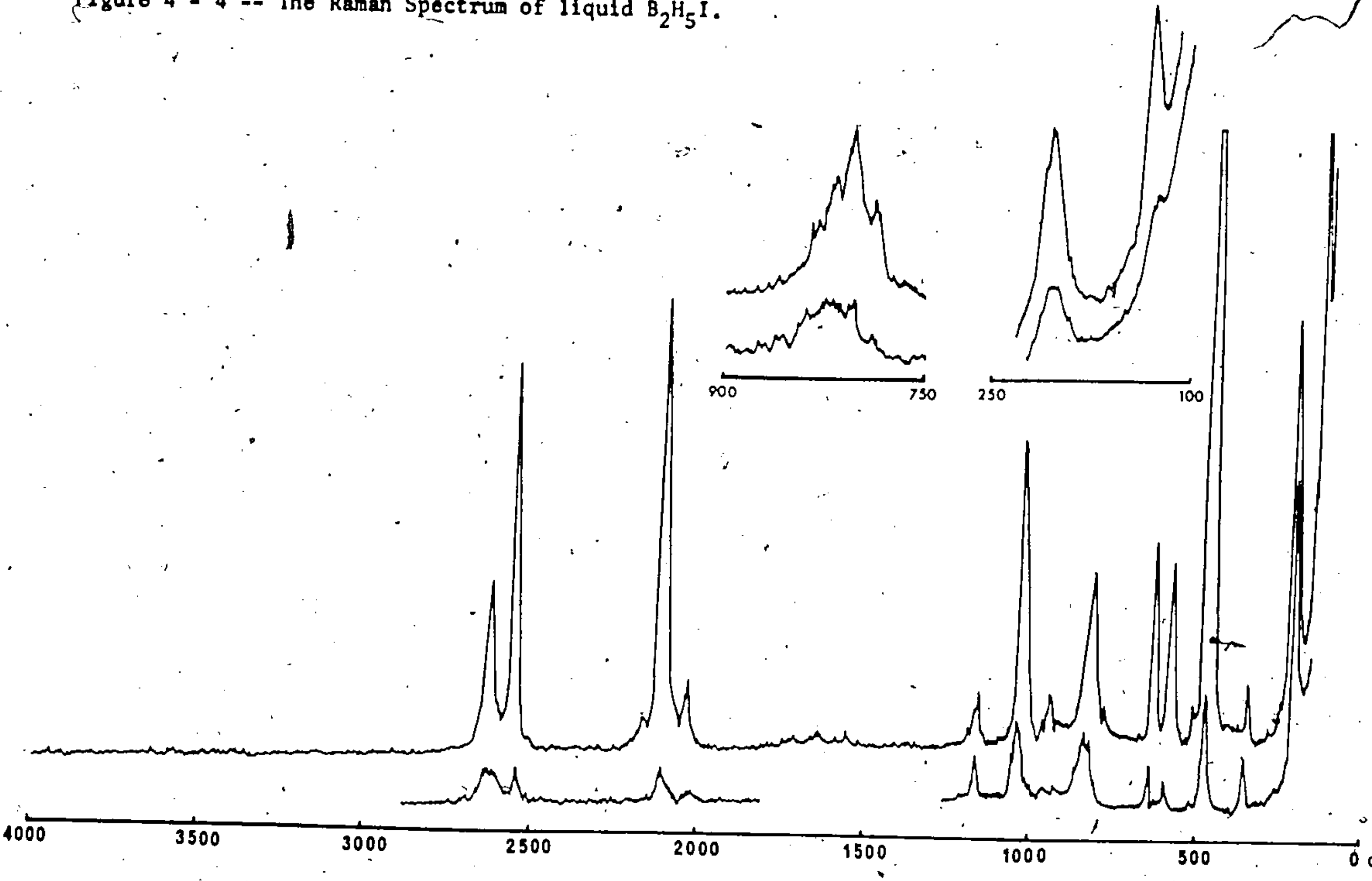


Figure 4 - 4 -- The Raman Spectrum of liquid B_2H_5I.

TABLE 4 - 4

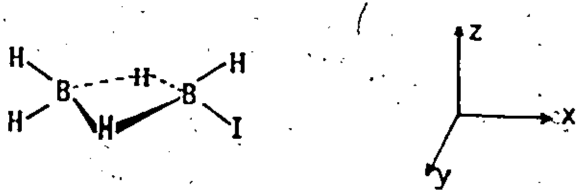
Correlated listing of all Infrared and Raman frequencies (cm^{-1}) for B_2H_5I

INFRARED			RAMAN		
3610	3640 3680	w	-		
2620	2610 2630	s	2590	m	p
2540		s	-		
2528		s	2517	s	p
2345	2320 2370	vw	-		
	-		2014	w	p
	-		2088	s	p
1880		w	-		
1735		m	-		
1580		vvw	1594	vvw	?
1440		m	-		
1272	1265 1280	w	-		
1165		s	-		
1151	-	s	1150	w	p(?)*
1029	1020 1038	vs	1014	s	p
936	942 930	w	941	w	p
910		w	-		
805	800 810	m	809	m	dp
631	640 622	w	622	m	p
570		vw	571	m	p
463		s	452	vvs	p
	-		341	w	dp
	-		205	s	dp(?)
	-		126	m	p

*This band is also of doubtful polarization in B_2H_5Me.

diborane, B_2H_6, is known to belong to symmetry group D_{2h}, with the four-membered B_2H_2 ring in a plane perpendicular to the four terminal hydrogen atoms. The ^1H and ^{11}B n.m.r. spectra of B_2H_5I are consistent with substitution of iodine for a terminal hydrogen. Hence, upon substitution the symmetry of the system is lowered to C_s. The geometry of the molecule is assumed to be as shown in Figure 4 - 5, where XZ is the symmetry plane.

Figure 4 - 5 -- The molecular structure of B_2H_5I



Since B_2H_5I is an eight-atom system, 18 fundamental vibrations are to be expected on the basis of 3n - 6 degrees of freedom for the non-linear case. Application of group theoretical considerations[44] leads to the expectation of 12 A' modes (in-plane vibrations) and 6 A" modes (out-of-plane vibrations), with the former being polarized and the latter depolarized in the Raman Effect. Since the system is of C_s symmetry all fundamentals should be both infrared and Raman active, although it sometimes happens that not all vibrations are observed in one or the other spectrum.

In addition to symmetry considerations, the previously assigned fundamentals of monomethyldiborane[34] were used in making assignments for monoiododiborane. As in the case of B_2H_5Me, the following infrared bands were eliminated as fundamental vibrations and assigned to various combinations and overtones of the B_2H_5- system: 3610, 2345, 1440, and

1272 cm^{-1}. None of these frequencies was observed in the Raman. Five other infrared bands were also not observed in the Raman spectrum. The unobserved Raman frequency corresponding to the 2528 cm^{-1} infrared band may be unresolved in the 2517 cm^{-1} Raman band. For the same reason the Raman counterparts of the 1165 and 910 cm^{-1} infrared vibrations may be part of unresolved neighboring bands. No Raman activity is seen to correspond to the 1880 and 1735 cm^{-1} infrared frequencies. The same phenomenon occurs in the B_2H_5Me spectrum. Yet both bands are used in the assignment of fundamentals because of their correspondence with the diborane spectrum.[20,42,45]

Aside from the three lowest Raman frequencies, which were outside the limits imposed by the infrared optics, only two bands were observed in the Raman which were not seen in the infrared spectrum. The weak polarized band at 2014 cm^{-1} may be an overtone of the intense absorption at 1014 cm^{-1}. The unobserved infrared frequency corresponding to the strong 2088 cm^{-1} Raman band is a condition identical to that in the B_2H_5Me spectra and may be too weak to observe.

The assignment of fundamental vibrational modes for the B_2H_5I system is given in Table 4 - 5. Since assignment was made not only on the basis of symmetry considerations, but also by comparison with the monomethyldiborane system, the corresponding B_2H_5Me frequencies are also reported. The assignments for the B_2H_5Br and B_2H_5Cl systems, also based on the methyl-substituted compound, were used only in assigning modes associated with the iodine atom.

TABLE 4 - 5

Fundamental vibrations (cm^{-1}) for B_2H_5X (X = I, Me)

ASSIGNMENT	B_2H_5I		B_2H_5Me	
	Ir	Raman	Ir	Raman
A' MODES				
BH_2 asym st	2620	2590	2571	2575
BH st	2540	2517	-	-
BH_2 sym st	2528	-	2519	2522
BH_b sym (in-phase) st	-	2088	-	2105
BH_b asym (in-phase) st	1580	1594	-	1592
BH_2 def	1165	-	1181	1168
BH (in-phase) bend	1151	1150	1136	-
BX st	1029	1041	-	995
BH_2 rock	936	941	-	-
B-B st	631	622	-	638
ring pucker	570	571	-	359
BX (in plane) bend	463	452	-	300(?)
A" MODES				
BH_b sym (out-of-phase) st	1880	-	1919	-
BH_b asum (out-of-phase) st	1735	-	1779	-
BH_2 waq	910	-	946	-
BH (out-of-plane) bend	805	809	901	-
BH_2 twist	-	341	-	-
BX (out-of-plane) bend	-	205	-	-

A few assignment differences between the two systems are to be noted. In the spectrum of B_2H_5Me, the 359 cm^{-1} band is assigned to the ring puckering mode as in diborane.[45] The only band corresponding to this frequency in the B_2H_5I spectrum is the 341 cm^{-1} absorption. But this band is clearly depolarized and can not be assigned to an A' mode. The 341 cm^{-1} band is therefore assigned to the A" BH_2 twist which was left unassigned in the spectrum of the corresponding methyl compound. Further, a polarized band at 576 cm^{-1} in the B_2H_5Me spectrum is reported but not assigned as a fundamental. It is this frequency which is now assigned as due to the ring pucker.

The BH_2 rock was also unassigned in the B_2H_5Me spectrum. The 940 cm^{-1} band is assigned to this fundamental mode in B_2H_5I. Its very clear polarization precluded assigning this frequency to tha A" BH_2 wag which is given a 946 cm^{-1} value (infrared only) in B_2H_5Me. The BH_2 wagging mode is now assigned to the weak infrared band at 910 cm^{-1} in the B_2H_5I spectrum.

On the basis of polarization data the 809 cm^{-1} band is assigned to the BH out-of-plane bend in contrast to the assignment some 100 cm^{-1} higher in B_2H_5Me. An absorption at 801 cm^{-1} in the latter spectrum is reported but not taken as a fundamental. No polarization data is given.

The 809 cm^{-1} region of the Raman spectrum of B_2H_5I is quite complex (see Figure 4 - 4) and probably is an area of some overtone and combination activity. Similarly the 1014 cm^{-1} peak, strong in both infrared and Raman and assigned to the BI stretch, may also contain the 571 + 452 cm^{-1} combination band. The corresponding difference band accounts for the 125 cm^{-1} peak.

It may be surprising that the BI stretch should be at a frequency higher than that of the BC stretching frequency in B_2H_5Me. However, this seems to be the case for all of the monohalodiboranes (Table 4 - 6). A generally uniform decrease in the BX stretching frequency is observed from the chloride through the iodide.

TABLE 4 - 6

The BX fundamental vibrations for the monohalodiboranes (cm^{-1}); infrared values only.

		B_2H_5Cl[23]	B_2H_5Br[23]	B_2H_5I
BX st	A'	1092 1073	1066 1051	1038 1020
BX bend	A'	847 831	818 807	463*
BX bend	A"			205*

*Raman frequencies

The frequency of the BX bend is much lower than those of the corresponding mode in the other two halide compounds, but the intensity of the 452 cm^{-1} band in the Raman can not be disregarded and must be assigned to a mode involving the iodine atom. Finally, the 205 cm^{-1} absorption is of doubtful polarization but the assignment of this band to the iodine out-of-plane bending mode does not seem unreasonable.

The splitting of several infrared bands is seen throughout the spectrum. This may reflect the effects of the ^{10}B-^{11}B isotopic distribution in some cases and in others, the three unequal moments of inertia possessed by the molecule. For molecules of symmetry lower than C_{2v}, D, or D_{2h}, the band contours become too complicated to permit any conclusions to be drawn concerning the symmetry species of specific fundamental vibrations.[47]

SECTION 5

VIBRATIONAL SPECTROSCOPIC DATA

1. The PH_3BCl_3 System.
2. The PH_3BBr_3 System.
3. The PH_3BI_3 System.
4. The PD_3BCl_3 Ststem.
5. The PD_3BBr_3 System.
6. The PD_3BI_3 System.

TABLE 8 - 1

A COMPREHENSIVE LISTING OF ALL VIBRATIONAL SPECTROSCOPIC DATA IN CM^{-1} ± 3 CM^{-1} FOR PH$_3$BCl$_3$

ASSIGNMENT	Solid (R)	CH$_3$I sol (R)	CH$_2$Cl$_2$ sol (R)	CsI pellet (IR)	Nujol mull (IR)	CH$_3$I sol (IR)	CH$_2$Cl$_2$ sol (IR)	COMPOSITE	DESCRIPTION
$\nu_7 + \nu_{11}$	2698 vw							2698	2447 + 242 = 2689
$\nu_7 + \nu_{12}$	2610 w							2610	2447 + 148 = 2595
ν_7	2447 s	2426 m dp	2445 m dp	2448 vvw	2440 m	2420 m	2441 w	2447	PH st (a)
ν_1	2412 vs	2396 vs p	2415 vs p	2415 vvw	2408 w	2380 w	2412 vw	2412	PH st (s)
$\nu_7 - \nu_{12}$	2296 w							2296	2447 - 148 = 2299
$\nu_7 - \nu_{11}$	2190 vw							2190	2447 - 242 = 2205
$2\nu_8$	2108 vvw							2108	2 x 1059 = 2118
$2\nu_2$	1952 w							1952	2 x 985 = 1970
$\nu_8 + \nu_9$	1772 w							1772	1059 + 730 = 1789
$\nu_8 + \nu_{10}$	1612 vw							1612	1059 + 560 = 1619
$2\nu_9$	1455 vw	solvent	solvent					1455	2 x 730 = 1460
$2\nu_3$	1382 w	solvent	solvent					1382	2 x 690 = 1380
$2\nu_{10}$	1118 w	1114 vw dp	1120 vw dp	1120 vw	1120 vvw	1118 vvw	1125 vw	1118	2 x 560 = 1120
ν_8	1061 s	1080 m dp(?)	1080 m dp	1064 s	1054 s	1098 m	1065 w	1059	PH def (a)
ν_2	981 m	988 w p(?)	988 w p	988 s	988 s	992 s	991 s	985	PH def (s)
$\nu_9(^{10}B)$	755 w	754 w dp(?)	solvent	750 sh		750 s		755	^{10}BCl st (a)
ν_9	730 m		solvent	729 s	721 s		738 s	730	BCl st (a)
$\nu_3(^{10}B)/\nu_{10} + \nu_{12}$	~700	700 vvw	solvent	700 w	705 w	705 m	701 s	702	^{10}BP st(s); 560+148=708
ν_3	693 m	675 m p(?)	solvent	675 m	675 m	675 s	675 s	675	PB st (s)
$\nu_4 + \nu_5$	640 m	680 vw	649 vvw	640 w		645 w	645 w	647	399 + 254 = 653
ν_{10}	560 m	solvent	556 w dp	553 m	552 m	555 s	555 s	560	PH rock (a)
$2\nu_5$	508 w	solvent						508	2 x 254 = 508
$2\nu_{11}$	470 vw	475 vw p	475 w p	480 vvw	480 vvw		470 vvw	475	2 x 242 = 484
$\nu_{10} - \nu_{12}$			410 w p	425 vw	420 vvw		418 vvw	416	560 - 148 = 412
ν_4	399 vs	400 vs p	399 vs p	395 m	392 m	400 w	399 w	399	BCl st (s)
$\nu_8 - \nu_9$	320 vvw							320	1059 - 730 = 329
ν_5	254 s	249 m p	250 m p	252 s	252 s			254	BCl def (s)
ν_{11}	244 s	239 m dp	240 m dp	240 sh				242	BCl def (a)
ν_{12} $\nu_4 - \nu_5$	148 w	145 vw dp	147 vw dp					148	BCl rock (a)
lattice	80 m							80	lattice

TABLE 5 - 2

A COMPREHENSIVE LISTING OF ALL VIBRATIONAL SPECTROSCOPIC DATA (IN $CM^{-1} \pm 3\ CM^{-1}$) FOR PH_3BBr_3

ASSIGNMENT	Solid (R)	CH_3I sol (R)	CH_2Cl_2 sol (R)	CsI pellet (IR)	Nujol mull (IR)	CH_3I sol (IR)	CH_2Cl_2 sol (IR)	COMPOSITE	DESCRIPTION
$\nu_7 + \nu_{11}$	2585 w							2588	2428 + 160 = 2588
$\nu_7 + \nu_{12}$	2540 vw							2540	2428 + 115 = 2543
ν_7	2428 s	2426 s dp	2444 s dp	2430 m		2420 m	2418 w	2428	PH st (e)
ν_1	2390 vs	2390 vs p	2411 vs p	2390 w		2390 w	2390 vw	2390	PH st (a)
$\nu_7 - \nu_{12}$	2318 vw		2311 vvw					2318	2428 - 115 = 2313
$\nu_7 - \nu_{11}$	2275 w							2275	2428 - 160 = 2268
$2\nu_2$	1947 w							1947	2 x 979 = 1958
$2\nu_3$	1384 vvw	solvent	solvent					1384	2 x 700 = 1400
$2\nu_3$	1383 vvw	solvent	solvent					1383	2 x 682 = 1364
$\nu_2 + \nu_4$	1290 vw	solvent	solvent					1290	979 + 282 = 1261
$\nu_8 + \nu_{11}$	1197 vw	solvent						1197	1043 + 160 = 1203
$2\nu_{10}$	1071 m	1070 m dp	1070 s dp(?)	1068 vw	1069 vw	1078 w	1070 w	(1070)	2 x 530 = 1060
ν_8	1048 m	1064 m dp	1054 m dp	1062 w	1046 w	1080 m	1052 w	1080 (1048)	PH def (e)
ν_2	977 m	978 m p	991 m p	982 m	986 m	984 s	995 vvw	979	PH def (a)
$\nu_9(^{11}B)$	720 sh	720 vw dp	solvent	722 sh	725 w	715 sh	718 sh	720	^{11}BBr st (e)
ν_9				700 s	700 s			700	BBr st (e)
$\nu_3(^{11}B)$	} 695 m	} 686 m p(?)	solvent	695 sh		} 695 s	} 690 s	695	^{11}BP st (a)
ν_3	675 sh	676 m p(?)	solvent	682 m	675 s	682 s		682	BP st (a)
ν_{10}	530 m	solvent	531 m dp	529 m	528 s	530 s	525 vvw	530	PH rock (e)
$\nu_4 + \nu_5$	478 vvw	solvent		480 vw	473 vvw	473 vvw	460 vw	467	282 + 182 = 464
ν_4	282 m	282 s p	solvent	281 w	280 s			282	BBr st (a)
$2\nu_{12}$	233 vvw	230 vvw p(?)	230 vw p					230	2 x 115 = 230
ν_5	183 w	181 vw p	181 vw p					182	BBr def (a)
ν_{11}	160 w	160 vw dp	154 vw dp(?)					160	BBr def (e)
ν_{12}	120 w	113 vw dp						115	BBr rock (e)
lattice	73 vw							73	lattice

TABLE 5 - 3

A COMPREHENSIVE LISTING OF ALL VIBRATIONAL SPECTROSCOPIC DATA IN CM^{-1} ± 3 CM^{-1} FOR PH_3BI_3

ASSIGNMENT	Solid (R)	CH_3I sol (R)	CH_2Cl_2 sol (R)	CsI pellet (IR)	Nujol mull (IR)	CH_3I sol (IR)	CH_2Cl_2 sol (IR)	COMPOSITE	DESCRIPTION
$\nu_7 + \nu_{11}$	2529 w							2529	2397 + 127 = 2527
$\nu_7 + \nu_{12}$	2490 vw	2485 vw p						2485	2397 + 89 = 2486
ν_7	2397 vs	2418 s dp	2432 s dp	2398 w	2398 vvw	2402 w	2402 w	2397	PH st (e)
ν_1	2362 vs	2378 vs p	2397 vs p	2365 w	2370 vvw	2390 w	2380 w	2364	PH st (a)
$\nu_7 - \nu_{12}$	2306 vvw	2310 vw p	2314 vw p(?)					2310	2397 - 89 = 2308
$\nu_7 - \nu_{11}$	2270 w							2270	2397 - 127 = 2270
$2\nu_2$	1945 vw							1948	2 x 981 = 1962
$2\nu_9$	1345 vw	solvent	solvent					1345	2 x 678 = 1360
$2\nu_3$	1309 vw	solvent	solvent	1280 w				1309	2 x 662 = 1324
$\nu_8 + \nu_{12}$	1160 vw		solvent	1150 w				1160	1058 + 89 = 1147
ν_8	1054 s	1060 m dp	1064 m dp	1058 m	1061 m	1056 m	1043 m	1056	PH def (e)
ν_2	981 m	980 w p	992 m p	981 s	981 s	988 s	992 s	981	PH def (a)
$\nu_9(^{10}B)$	706 w		solvent	700 sh		690 sh		700	^{10}BI st (e)
$\nu_3(^{11}B)$								680	^{11}BP st (a)
	) 678 m	) 680 m (?)							
ν_9			671 m dp	670 s	671 s	675 m	) 680 s	678	BI st (e)
ν_3	651 m	647 m p(?)	659 m p(?)	643 s	643 s	660 vs	665 s	662	BP st (a)
$\nu_{10} + \nu_{12}$		solvent	575 vw p	560 w	570 w	552 w		570	492 + 89 = 581
ν_{10}	492 s	solvent	496 m dp	491 s	487 s	491 vs	492 m	492	PH rock (e)
$2\nu_4$	460 w	solvent	427 vw p		420 w			460	2 x 230 = 460
$\nu_4 + \nu_5$	363 w	367 vw p	372 vw p	370 vvw		355 vw		360	230 + 134 = 364
$\nu_4 + \nu_{12}$	307 vw	320 vw p	solvent	320 vvw		318 vw		318	230 + 89 = 319
ν_4	229 m	230 m p	solvent	232 m	232 m			230	BI st (a)
ν_5	136 m	133 m p	131 m p					134	BI def (a)
ν_{11}	127 sh	127 w dp	129 w dp					127	BI def (e)
ν_{12}	89 s	89 w dp	87 w dp					89	BI rock (e)
lattice	29 m							29	lattice

TABLE 5 - 4

A COMPREHENSIVE LISTING OF ALL VIBRATIONAL SPECTROSCOPIC DATA IN CM^{-1} $\pm$ 3 CM^{-1} FOR PO$_3$BCl$_3$

ASSIGNMENT	Solid (R)	CH$_3$I sol (R)	CH$_2$Cl$_2$ sol (R)	CsI pellet (IR)	Nujol mull (IR)	CH$_3$I sol (IR)	CH$_2$Cl$_2$ sol (IR)	COMPOSITE	DESCRIPTION
$\nu_7 + \nu_{11}$	2030 vvw							2030	1787 + 241 = 2028
$\nu_7 + \nu_{12}$	1938 vw							1938	1787 + 154 = 1941
ν_7	1787 s	1770 s dp	1789 s dp	1790 w		1770 w	1780 vw	1787	PO st (e)
ν_1	1743 vs	1730 vs p	1744 vs p	1745 vw		1745 vw	1740 vw	1743	PO st (a)
$\nu_7 - \nu_{12}$	1647 vvw							1647	1787 - 154 = 1633
$2\nu_2$	1560 vvw							1560	2 x 780 = 1560
$2\nu_9$	1440 vw	solvent	solvent					1440	2 x 718 = 1436
$\nu_9 + \nu_3$	1352 vvw	solvent	solvent			1360 w		1352	718 + 633 = 1351
$2\nu_3$	1250 vw	solvent	solvent					1250	2 x 633 = 1266
$\nu_8 + \nu_{10}$	1215 vw		solvent					1215	774 + 440 = 1214
$\nu_2 + \nu_{12}$	912 w		905 w dp	930 w	911 m	930 m		912	785 + 144 = 929
$2\nu_{10}$	880 vw		solvent	880 w		880		880	2 x 440 = 880
ν_8	774 m	775 m dp(?)	solvent	775 m	764 s	775 sh		774	PO def (e)
ν_2	~780 sh	780 sh p	solvent	785 sh		785 s		785	PO def (a)
ν_9	718 w	725 w dp(?)	solvent	720 s	720 s	720 s		718	BCl st (e)
$\nu_3(^{10}B); \nu_4 + \nu_5$	647 w	680 w p(?)	solvent	658 m	647 s	665 w	660 sh	656	^{10}BP st (a)
ν_3	632 w	633 w p	630 w p(?)	635 m	635 sh	620 w	640 s	633	BP st (a)
$2\nu_{11}$	489 w	solvent	480 vw p	490 w	484 w	480 vw	480 w	489	2 x 241 = 482
ν_{10}	441 s	solvent	440 m dp	440 w	438 m	438 vw	434 m	440	PO rock (e)
ν_4	395 vs	399 vs p	397 vs p	395 vw	395 w	390 vw		395	BCl st (a)
$\nu_8 - \nu_{10}$	352 vw							352	774 - 440 = 334
$2\nu_{12}$	295 vw		solvent	310 w				295	2 x 154 = 308
ν_5	247 s	244 m p	248 m p(?)	249 vw	253 w			247	BCl def (a)
ν_{11}	241 s	235 m dp		238 w	238 w			238	BCl def (e)
$\nu_{12}; \nu_4 - \nu_5$	144 w		143 vw dp					144	BCl rock (e) 395 - 252 = 143
lattice	79 w							79	lattice

TABLE 5 - 5

A COMPREHENSIVE LISTING OF ALL VIBRATIONAL SPECTROSCOPIC DATA IN CM^{-1} ± 3 CM^{-1} FOR PO$_3$BBr$_3$

ASSIGNMENT	Solid (R)	CH$_3$I sol (R)	CH$_2$Cl$_2$ sol (R)	CsI pellet (IR)	Nujol mull (IR)	CH$_3$I sol (IR)	CH$_2$Cl$_2$ sol (IR)	COMPOSITE	DESCRIPTION
$\nu_7 + \nu_{11}$	1930 w							1930	1773 + 150 = 1923
$\nu_7 + \nu_{12}$	1890 w	1902 w dp	1892 w dp					1892	1773 + 112 = 1885
ν_7	1773 s	1772 s dp	1783 s dp	1768 m	1770 m	1760 w	1770 vw	1772	PO st (e)
ν_1	1726 vs	1727 vs p	1734 vs p	1730 w	1735 w	1730 vw		1726	PO st (a)
$\nu_7 - \nu_{12}$	1672 w	1676 w dp(?)	1682 w dp(?)					1672	1773 - 112 = 1661
$\nu_7 - \nu_{11}$	1625 w	1624 w						1625	1773 - 150 = 1623
$2\nu_2$	1516 vw							1516	2 x 760 = 1520
$2\nu_9$	1330 vw							1330	2 x 663 = 1326
$2\nu_3$	1287 vw							1287	2 x 650 = 1300
$\nu_2 + \nu_5$	940 w	948 m dp	950 w dp	940 vw	945 m	950 w	950 w	948	760 + 181 = 941
$\nu_8 + \nu_{11}$	898 w	902 m dp	900 w dp	901 w	892 m	900 m	902 m	901	760 + 150 = 910
$2\nu_{10}$	843 w		845 vw p(?)					845	2 x 428 = 856
ν_8	780 m	765 m (?)	solvent	770 sh				780	PO def (e)
ν_2	780 m	765 m (?)	solvent	760 w	}753 m	} 760 m	} 762 m	780	PO def (a)
$\nu_9(^{10}B)$	678 w	} 665 m dp(?)	} 651 w dp(?)	675 sh		680 sh	680 sh	678	^{10}BBr st (e)
ν_9	663 m			660 m	665 m	670 s	670 s	663	BBr st (e)
$\nu_3(^{10}B)$	} 640 m	} 642 m p	} 638 w p(?)	650 sh				650	^{10}BP st (a)
ν_3				630 m	}640 m	} 661 s	} 661 s	634	BP st (a)
$2\nu_4$		solvent	540 w dp	530 m				540	2 x 278 = 556
$\nu_4 + \nu_5$	471 w	solvent	472 w dp	470 w	465 w	470 m	469 m	468	278 + 181 = 459
ν_{10}	431 m	430 m dp	431 m dp	431 m	418 s	428 m	426 m	428	PO rock (a)
$2\nu_5$	360 w	355 vw p	370 vw p	350 w				360	2 x 181 = 362
$\nu_5 + \nu_{12}$	325 w	323 vw p	solvent	315 w				325	181 + 150 = 331
ν_4	272 m	280 s p	solvent	278 m	272 m			278	BBr st (a)
ν_5	182 m	181 w p	182 m p					181	BBr def (a)
ν_{11}	155 m	150 w dp	147 w dp					150	BBr def (e)
ν_{12}	112 w		112 w dp					112	BBr rock (e)
lattice	72 m							72	lattice

TABLE 5 - 6

A COMPREHENSIVE LISTING OF ALL VIBRATIONAL SPECTROSCOPIC DATA IN CM^{-1} ± 3 CM^{-1} FOR PD$_3$BI$_3$

ASSIGNMENT	Solid (R)	CH$_3$I sol (R)	CH$_2$Cl$_2$ sol (R)	CsI pellet (IR)	Nujol mull (IR)	CH$_3$I sol (IR)	CH$_2$Cl$_2$ sol (IR)	COMPOSITE	DESCRIPTION
$\nu_7 + \nu_{11}$	1879 vw							1879	1752 + 123 = 1875
$\nu_7 + \nu_{12}$	1846 vw							1845	1752 + 89 = 1841
ν_7	1772 s	1760 s dp	1770 s dp	1750 vw	1765 vw	1755 vw		1752	PD st (e)
ν_1	1709 vs	1713 vs p	1720 vs p	1709 vw		1718 vw		1709	PD st (a)
$\nu_7 - \nu_{12}$	1662 vw							1662	1752 - 89 = 1663
$\nu_7 - \nu_{11}$	1638 vvw							1638	1752 - 123 = 1629
$2\nu_2$	1515 vw							1515	2 x 762 = 1524
$2\nu_9$	1182 vw	solvent	solvent					1182	2 x 596 = 1192
$\nu_2 + \nu_4$	970 vvw			978 w				978	760 + 220 = 980
$\nu_2 + \nu_5$	880 vw			901 w	895 w	900 m	895 m	895	760 + 133 = 893
$2\nu_{10}$	826 vw			825 w	825 w			826	2 x 418 = 836
ν_8	} 760 m	768 m dp(?)	solvent	762 sh	} 759 s	} 763 s	} 770 s	762	PD def (e)
ν_2		760 m p(?)	solvent	760 s				760	PD def (a)
$\nu_3(^{10}B)$	659 w				658 sh			657	^{10}BP st (a)
ν_3	642 m	641 m p(?)	solvent	649 s	642 s	645 m	650 w	642	BP st (a)
$\nu_9(^{10}B)$	615 w	609 w (?)	625 w dp	620 m	615 s	620 w	615 w	613	^{10}BI st (e)
ν_9	598 m	590 m dp(?)	605 w dp	600 s	595 s	595 s	598 s	596	BI st (e)
$2\nu_4$	448 w			455 w	450 w	455 w	458 w	448	2 x 220 = 440
ν_{10}	418 s	420 m dp	425 m dp(?)	420 m	410 s	420 m	420 m	418	PD rock (e)
ν_4	220 vs	222 s p	228 s p	225 w	220 m			220	BI st (a)
ν_5	134 s	132 w p	135 m p					133	BI def (a)
ν_{11}	123 m							123	BI def (e)
ν_{12}	89	89 vw dp	89 vw dp					89	BI rock (e)

REFERENCES

1. D. F. Shriver, "The Manipulation of Air-Sensitive Compounds," McGraw-Hill Book Co., New York, 1969, pp. 1 - 6.

2. W. L. Jolly, "Synthetic Inorganic Chemistry," Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1960, pp. 94 - 101.

3. R. E. Rondeau, J. Chem. Educ., 42, A445 (1965).

4. R. E. Rondeau, ibid., 42, A511 (1965).

5. D. F. Shriver, op. cit., pp. 8 - 9.

6. W. L. Jolly, op. cit., pp. 105 - 107.

7. A. H. Van Geet, Anal. Chem., 40, 2227 (1968).

8. A. H. Cowley and M. C. Damasco, J. Amer. Chem. Soc., 93, 6815 (1971).

9. G. Herzberg, "Molecular Spectra and Molecular Structure, II. Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., Princeton, New Jersey, 1968, p. 311.

10. A. E. Finholt, A. C. Bond, K. E. Wilzbach, and H. I. Schlessinger, J. Amer. Chem. Soc., 69, 2692 (1947).

11. E. Lee and C. K. Wu, Trans. Faraday Soc., 35, 1366 (1939).

12. W. L. Jolly, Inorganic Synthesis, 11, 124 (1968).

13. J. A. Lannon and E. R. Nixon, Spectrochim. Acta, 23A, 2713 (1967).

14. G. M. Whitesides, J. L. Beauchamp, and J. D. Roberts, J. Amer. Chem. Soc., 85, 2665 (1963).

15. S. L. Manatt, G. L. Juvinall, R. I. Wagner, and D. D. Elleman, ibid., 88, 2689 (1966).

16. W. L. Jolly, Inorganic Synthesis, 11, 126 (1968).

17. H. C. Beachall and B. Katlafsky, J. Chem. Phys., 27, 182 (1957).

18. A. I. Vogel, "A Textbook of Practical Organic Chemistry," 3rd ed., Longmans, London, 1959, p. 182,

19. H. G. Weiss and I. Shapiro, J. Amer. Chem. Soc., 81, 6167 (1959).

20. R. C. Lord and E. Nielse, J. Chem. Phys. 19, 1 (1951).

21. H. I. Schlesinger and A. B. Burg, J. Amer. Chem. Soc., 53, 4321 (1931).

22. J. Bouis and J. Cueilleron, Bull. Soc. Chim. Fr., 3157 (1968).

23. S. B. Rietti and J. Lombardo, J. Inorg. Nucl. Chem., 27, 247 (1965).

24. D. F. Gaines and R. Schaeffer, J. Phys. Chem., 68, 955 (1964).

25. A. Stock and E. Pohland, Chem. Ber., 59, 2223 (1926).

26. J. Cueilleron and H. Mongeot, Bull. Soc. Chim. Fr., 1065 (1967).

27. V. M. McConaghie and H. H. Nielsen, J. Chem. Phys., 21, 1836 (1953).

28. H. C. Brown and R. B. Johannesen, J. Amer. Chem. Soc., 72, 2173 (1950).

29. D. M. Cage and E. F. Barker, J. Chem. Phys., 7, 455 (1939).

30. H. C. Brown and R. R. Holmes, J. Amer. Chem. Soc., 78, 2173 (1956).

31. R. F. Scruby, J. R. Lacher, and J. D. Parks, J. Chem. Phys., 19, 386 (1951).

32. T. Wentick and V. H. Tiensuu, ibid., 28, 826 (1958).

33. J. Cueilleron and H. Mongeot, Bull. Soc. Chim. Fr., 76 (1966).

34. J. H. Carpenter, W. J. Jones, R. W. Jotham, and L. H. Long, Spectrochim. Acta, 27A, 1721 (1971).

35. J. H. Carpenter, W. J. Jones, R. W. Jotham, and L. H. Long, ibid., 26A, 1199 (1970).

36. D. F. Shriver, op. cit., p. 70.

37. S. Glasstone and D. Lewis, "Elements of Physical Chemistry," D. Van Nostrand Co., Inc., Princeton, New Jersey, 1960, p. 138.

38. R. A. Ogg, J. Chem. Phys., 22, 1955 (1954).

39. J. N. Shoolery, Disc. Faraday Soc., 19, 215 (1955).

40. W. D. Phillips, H. C. Miller, and E. L. Muetterties, J. Amer. Chem. Soc., 81, 4496 (1959).

41. D. F. Gaines, Inorg. Chem., 2, 523 (1963).

42. W. C. Price, J. Chem. Phys., 16, 894 (1948).

43. K. Hedberg and V. Schomaker, J. Amer. Chem. Soc., 73, 1482 (1951).

44. H. H. Jaffe and M. Orchin, "Symmetry in Chemistry." John Wiley and Sons, Inc., New York, 1967, p. 172.

45. W. L. Smith and I. M. Mills, J. Chem. Phys. 41, 1479 (1964).

46. W. H. Lehmann, C. O. Wilson, and I. Shapiro, ibid., 32, 1088 (1960).

47. N. L. Alpert, W. E. Keiser, and H. A. Szymanski, "IR Theory and Practice of Infrared Spectroscopy," 2nd ed., Plenum Press, New York, 1970, p. 157.

VITA

Born -- St. Louis, Missouri, USA	June 12, 1933
Entered the Teaching Congregation of the Brothers of the Christian Schools (the De La Salle Brothers)	August 30, 1951
B. Sc. (Honors), St. Mary's College, Winona, Minnesota	May, 1955
M. Ed., St. Mary's College, Winona, Minnesota	May, 1962
M. Sc., Loyola University, Chicago, Illinois	February, 1970
Teaching Experience -- Teacher of secondary school chemistry in the schools of the Christian Brothers in Kansas City, Missouri; Minneapolis and St. Paul, Minnesota; Hammond, Indiana; and Lombard, Illinois	1955 - 1970
Awards -- National Science Foundation grants for In-Service Study:	
College of St. Thomas, St. Paul, Minn.	1958 - 1961
University of Minnesota, Minneapolis, Minn.	1964
Illinois Institute of Technology, Chicago, Ill.	1965 - 1968