THE RELATIVE ACCEPTOR POWER OF BORON TRIHALIDES AND BORANE TOWARD TRIMETHYLAMINE BY PROTON N.M.R. MEASUREMENTS

J. M. Miller and M. Onyszchuk

THE RELATIVE ACCEPTOR POWER OF BORON TRIHALIDES AND BORANE TOWARD TRIMETHYLAMINE BY PROTON N.M.R. MEASUREMENTS[1]

J. M. MILLER[2] AND M. ONYSZCHUK
Inorganic Chemistry Laboratory, McGill University, Montreal, Quebec

Received January 29, 1964

ABSTRACT

Proton n.m.r. spectra of trimethylamine adducts of the boron trihalides and borane have been measured in chloroform solution. Chemical shifts of methyl protons relative to tetramethylsilane decrease in the order: $BBr_3 > BCl_3 > BH_3 > BF_3$, suggesting that this is the order of acceptor activity toward trimethylamine. This is supported by the existence of a linear relationship between methyl proton chemical shifts and the heats of formation, dipole moments, or infrared vibrational shifts of boron trihalide and borane adducts. Splitting of methyl proton resonances into quartets have been observed for $(CH_3)_3N \cdot BCl_3$ and $(CH_3)_3N \cdot BBr_3$ but not for $(CH_3)_3N \cdot BF_3$ and $(CH_3)_3N \cdot BH_3$.

INTRODUCTION

Nuclear magnetic resonance measurements have been used recently to determine relative stabilities of BX_3 (where X = F, H, CH_3, or C_2H_5) addition compounds (1–8). Relative basicities of donor molecules and relative acceptor powers of BX_3 molecules have been inferred from such data. Calorimetric (9, 10), dipole moment (11), infrared (12, 13), and displacement reaction (14) measurements have shown recently that the relative acceptor power of boron trihalides toward a variety of donor molecules is $BBr_3 > BCl_3 > BF_3$. Methyl proton chemical shifts of their trimethylamine adducts should also indicate this order. The measurements reported here were made to examine this possibility.

RESULTS AND DISCUSSION

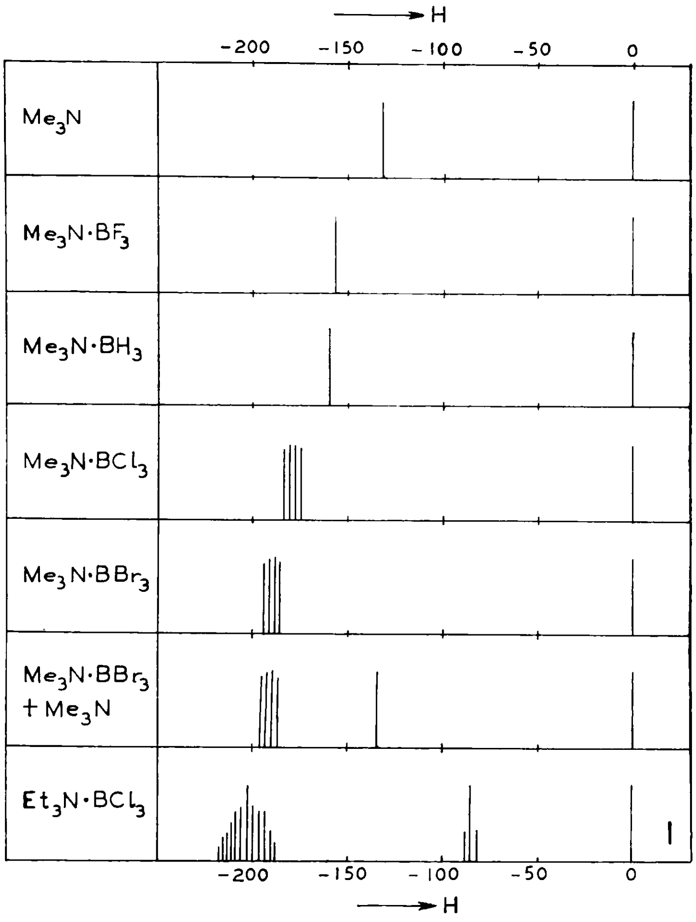
Chemical shifts of methyl protons in trimethylamine adducts of boron trihalides and borane were found to decrease in the order: $BBr_3 > BCl_3 > BH_3 > BF_3$. The measured values for 1 mole % solutions of the adducts in chloroform were 190.8, 180.2, 159.5, and 157.3 c.p.s., respectively, below the proton resonance of dilute tetramethylsilane ($\delta = 0$ c.p.s.). The corresponding proton chemical shift of trimethylamine in chloroform was 132.2 c.p.s. Line diagrams of the measured spectra are compared in Fig. 1. Chemical shifts were affected to an extent of only 1 or 2 c.p.s. by changes of concentration in the range of 1.0 to 0.2 mole %. The difference between chemical shifts of the BH_3 and BF_3 adducts was only 2.2 c.p.s. in chloroform solution, but this appears to be significant because almost the same effect was obtained for measurements in benzene solution.

The observed order of decrease in chemical shift can be rationalized as follows. If the acceptor power increases progressively from BF_3 to BBr_3, the electron pair of the B–N bond of the trimethylamine complex should be drawn progressively closer to the boron atom. The resulting decrease in electron density at the nitrogen atom should be compensated in part by electron release from the attached methyl groups. This effect, in turn, should result in a decrease in the electron density about the methyl protons and their shielding should be reduced. Consequently, proton resonances should shift to lower field

---

[1] *This work was supported by a grant from the Defence Research Board of Canada (Grant number 9530-20, Project D46-95-30-20).*

[2] *Holder of an N.R.C. Bursary, 1961–1962, and N.R.C. Studentships, 1962–1964.*



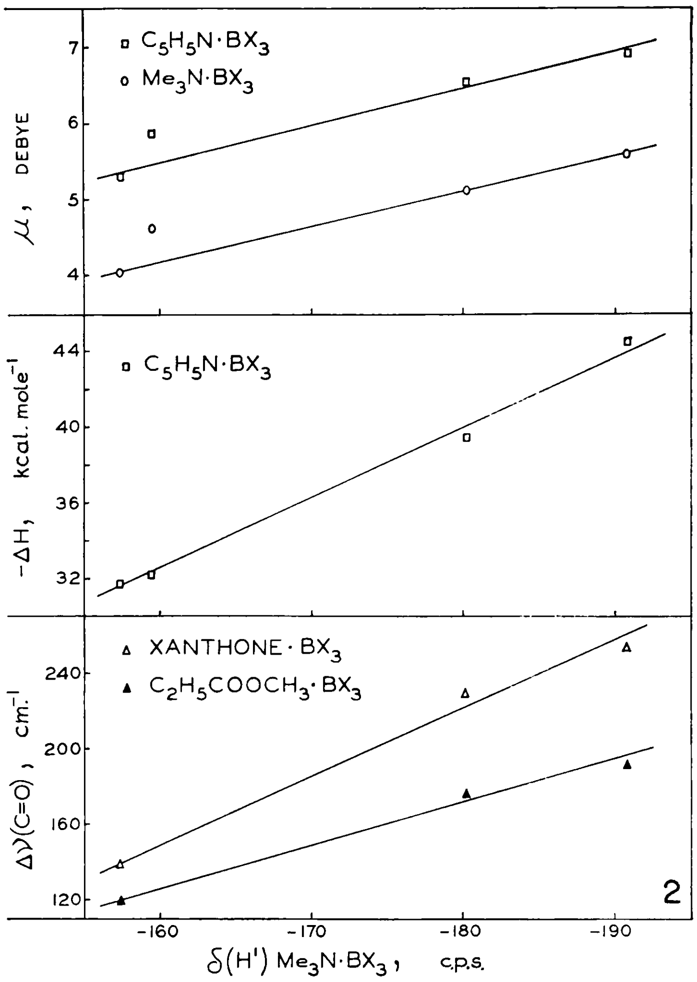


FIG. 1. Methyl proton n.m.r. spectra of $Me_3N \cdot BX_3$ (where X = H, F, Cl, Br) and $Et_3N \cdot BCl_3$.

FIG. 2. Correlations of methyl proton chemical shifts ot $Me_3N \cdot BX_3$ with dipole moments, heats of formation, and infrared carbonyl shifts of various BX_3 complexes.

as the electron acceptor power of the boron species increases. Since methyl proton chemical shifts decreased in the order $BBr_3 > BCl_3 > BH_3 > BF_3$, we conclude that this is also the order of acceptor power toward trimethylamine.

The above explanation may not be the only one. Changes in electronegativity and (or) magnetic anisotropy due to substitution of one halogen atom for another might account for the observed order. Several workers (15, 16) have suggested that in some *n*-haloalkanes these effects produce shifts to lower field in the order I > Br > Cl > F for β protons and the opposite order for α protons. However, in the case of isopropyl halides the order in α and β proton chemical shifts is I > Br > Cl > F, whereas the reverse order applies for α protons in *n*-propyl halides. These unusual shifts have yet to be explained satisfactorily. Dr. M. A. Whitehead and his co-workers in this department are now trying to estimate theoretically the relative magnitudes of inductive, magnetic anisotropy, and hyperconmoment (11) measurements which indicate that BH_3 is a slightly stronger acceptor than BF_3.

As shown in Table I and Fig. 2, linear relationships exist between our chemical shift data and dipole moments, heats of formation, and infrared shifts of various BX_3 (where X = H, F, Cl, Br) complexes, even though these values refer to different donor molecules. These linear correlations strongly suggest that proton chemical shifts reflect the same fundamental property of the complexes as do dipole moments, heats of formation, and infrared shifts. The property in common is probably the strength of the donor–acceptor bond, which, as suggested by Bax *et al.* (11) increases progressively from BF_3 to BBr_3 adducts because of a corresponding decrease in halogen valence shell electron-pair repulsions in the same order. Calorimetric and displacement results have been explained in terms of dative π-bonding and reorganization energies of boron trihalides (17, 14). This explanation cannot be used to account for dipole moment, infrared, and proton n.m.r. results because these data refer to properties of the complexes themselves and not to the energetics of their formation, as do heats of formation and displacement data. It is clear, nevertheless, that proton n.m.r. shifts, like heats of formation, dipole moments, and infrared shifts, indicate a relative acceptor power order of $BBr_3 > BCl_3 > BH_3 > BF_3$. Although displacement reaction studies showed that BF_3 is a slightly stronger acceptor than B_2H_6, it was evident that by taking the dimerization energy of BH_3 into account, BH_3 should be a stronger acceptor than BF_3. This expectation is confirmed by dipole moment, heat of formation, and our proton n.m.r. measurements.

TABLE I

Physical data for some BX_3 complexes

Property	Complex				Ref.
	BF_3	BH_3	BCl_3	BBr_3	
$-\Delta H$, kcal mole^{-1}, for $C_5H_5N(l) + BX_3(l)$ in $C_6H_5NO_2$ solution	31.7	32.2*	39.5	44.5	9, 10
Dipole moment, debye,					
$Me_3N \cdot BX_3$	4.04	4.62	5.13	5.57	11
$C_5H_5N \cdot BX_3$	5.31	5.86	6.52	6.90	11
Infrared shift, $\Delta\nu(C{=}O)$, cm^{-1}					
$C_2H_5COOCH_3 \cdot BX_3$	119	—	176	191	12
Xanthone·BX_3	138	—	229	253	13
Methyl proton chemical shift, δ c.p.s. $Me_3N \cdot BX_3$	157.3	159.5	180.2	190.8	this work

*Corrected for the dimerization energy of BH_3.

Methyl proton n.m.r. spectra $Me_3N \cdot BH_3$ and $Me_3N \cdot BF_3$ consisted (Fig. 1) of slightly broadened singlets, whereas $Me_3N \cdot BCl_3$ and $Me_3N \cdot BBr_3$ gave quartets with peaks of almost equal intensity and a splitting constant $J = 2.7$ and 2.8 c.p.s., respectively (Fig. 3). These splittings were independent of concentration in the range 1.0 to 0.2 mole % and were the same in chloroform, *o*-dichlorobenzene, and benzene solutions. Chemical shifts for $Me_3N \cdot BCl_3$ and $Me_3N \cdot BBr_3$ were measured from the center of each quartet. Each peak of the quartet appeared to be a closely spaced doublet with $J \simeq 0.7$ c.p.s. Ohashi *et al.* (6) have also observed a quartet for $Me_3N \cdot BCl_3$ with a splitting constant of 2.6 c.p.s., in excellent agreement with our value. However, they did not detect further splitting of the quartet into doublets. They also reported that the peak at highest field was weaker than the other three. We found this effect depended upon the

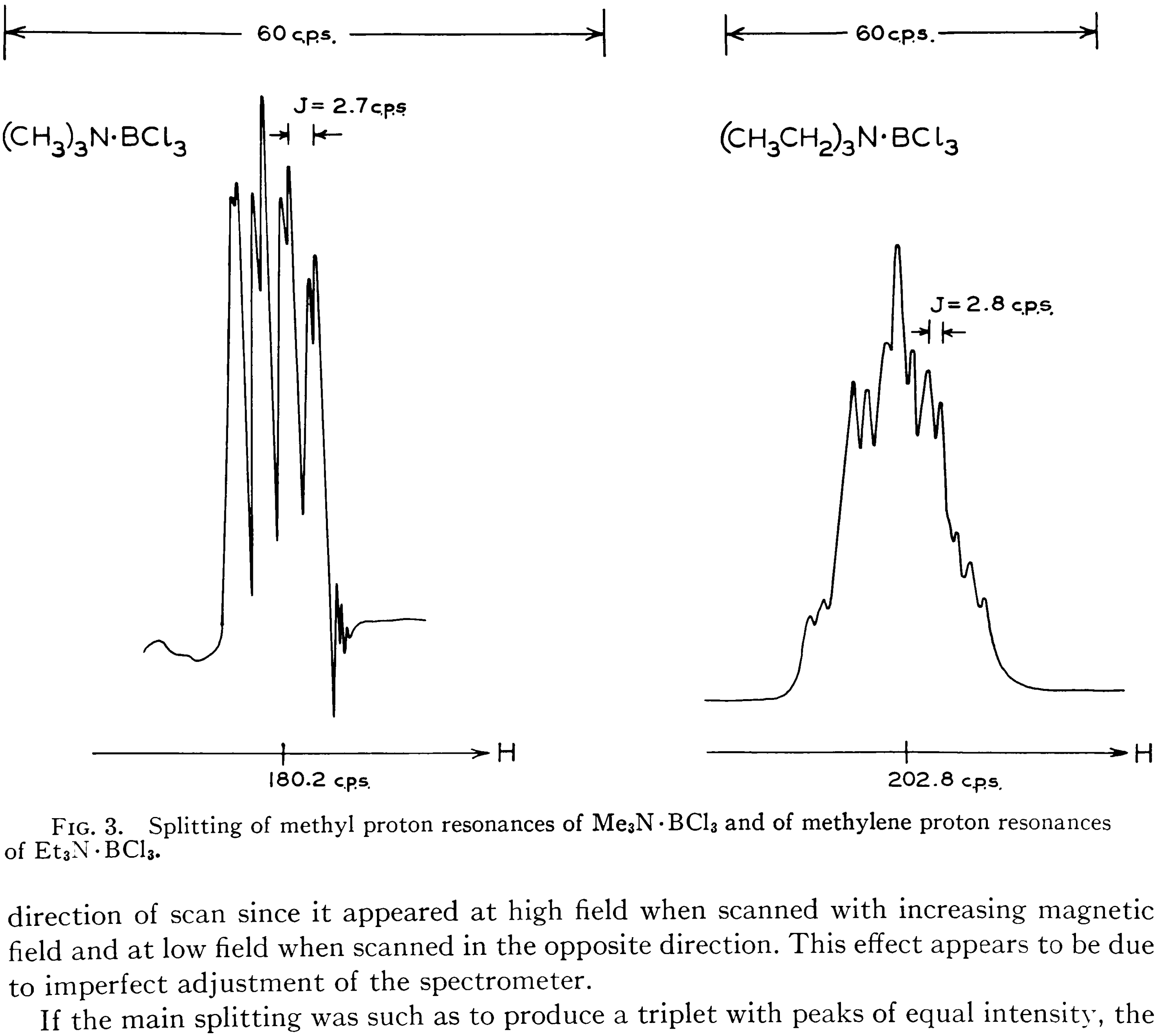


FIG. 3. Splitting of methyl proton resonances of $Me_3N{\cdot}BCl_3$ and of methylene proton resonances of $Et_3N{\cdot}BCl_3$.

direction of scan since it appeared at high field when scanned with increasing magnetic field and at low field when scanned in the opposite direction. This effect appears to be due to imperfect adjustment of the spectrometer.

If the main splitting was such as to produce a triplet with peaks of equal intensity, the effect could be ascribed to N^{14} spin–spin splitting, as has been proposed for anhydrous ammonia (18), $(CH_3CH_2)_4N^+I^-$ in D_2O solution (19), $(CH_3CH_2)_4N^+X^-$ (where X is Cl, Br, or OH) in Me_2SO, CH_3CN, and D_2O solution (19), and $(CH_3CH_2)_4N^+Br^-$ in H_2SO_4 solution (20). The same explanation has been suggested by Ohashi *et al.* (6) for the splittings in $Me_3N{\cdot}BCl_3$, even though they observed a quartet rather than a triplet. We think that N^{14} spin–spin coupling must be ruled out, because we observed quartets rather than triplets for $Me_3N{\cdot}BCl_3$ and $Me_3N{\cdot}BBr_3$.

Another possibility is coupling of methyl protons to B^{11} (spin 3/2) which should give a quartet with peaks of equal intensity. This effect should be just as likely to occur in $Me_3N{\cdot}BH_3$ and $Me_3N{\cdot}BF_3$ as in $Me_3N{\cdot}BCl_3$ and $Me_3N{\cdot}BBr_3$, but splittings were observed for the last two only. Perhaps restricted rotation about the B–N bond is necessary for coupling to be appreciable. Spatial models (of the Courtauld type) reveal that free rotation about the B–N bond is drastically restricted in $Me_3N{\cdot}BCl_3$ and $Me_3N{\cdot}BBr_3$ but not in $Me_3N{\cdot}BF_3$ and $Me_3N{\cdot}BH_3$. Hindered rotation might affect the electric field in such a way as to promote coupling of methyl protons with B^{11} and thereby give a quartet. An unambiguous test for B^{11} coupling could be made by double irradiation at the B^{11} resonance frequency. This test would be positive if a single methyl proton peak resulted. Unfortunately, we do not have the equipment to make this test. In an attempt to examine the possibility of hindered rotation in $Me_3N \cdot BCl_3$, its proton resonance spectrum was measured at temperatures between 25 and 100°. There was no detectable change.

The observed quartets could conceivably be caused by coupling of methyl protons with chlorine and bromine, both of which have nuclear spins of 3/2, in the hindered molecules. However, this is unlikely because these nuclei do not normally produce first-order splitting of proton resonances in organic compounds. Moreover, three halogens should produce splittings more complex than a quartet. Further splitting of each peak of the quartet into a doublet might be due to non-equivalence of the methyl groups arising from a loss of axial symmetry along the B–N bond in the sterically hindered BBr_3 and BCl_3 adducts. Less likely is the possibility that spin coupling to B^{10} (present as 20% of natural boron, spin 3) superimposes new lines on the quartets. Such coupling should produce more complex splitting than the well-defined doublets observed. The same objection should apply to an explanation involving spin coupling of methyl protons to the Cl^{35},Cl^{37} and Br^{79},Br^{81} isotopic pairs (spin 3/2).

We observed that $Me_3N \cdot BBr_3$ and excess Me_3N in chloroform solution gave two separate methyl proton resonances, one for the free amine and the other for the complex. This clearly shows that there is no or only very slow exchange of BBr_3 between Me_3N molecules. The quartet splitting constant and chemical shift was unaffected by the excess Me_3N.

No unusual splitting of ethyl proton resonances in BH_3, BF_3, and BMe_3 complexes of triethylamine were reported by Coyle and Stone (5), and none for $Et_3N \cdot BCl_3$ by Ohashi *et al.* (6). We found that $Et_3N \cdot BCl_3$ in chloroform solution gave a methyl proton triplet centered at 84.3 c.p.s. and a complex band (Fig. 3) centered at 202.8 c.p.s. where methylene resonances are expected. The latter has 12 distinct inflections, but may well have more buried in the complex envelope. A splitting of the expected 1:3:3:1 methylene quartet into 12 peaks is expected if N^{14} spin–spin coupling occurred, and into 16 for B^{11} coupling. We are unable to decide between these possibilities. It is interesting to note that in $Et_4N^+I^-$ the methyl triplet and not the methylene quartet is split, and this has been attributed to N^{14} spin–spin coupling (19). Such coupling does not occur in $Me_3NH^+Br^-$ and $Et_3NH^+Br^-$, the spectra of which in H_2O (19) and chloroform solution show no unusual splitting.

EXPERIMENTAL

Materials

Trimethylamine complexes of BH_3, BF_3, BCl_3, and BBr_3 were prepared and purified as described previously (14). A solution of $Et_3N \cdot BCl_3$ in chloroform was prepared by bubbling BCl_3 (Matheson) into a solution of Et_3N (Eastman) in chloroform. Triethyl and trimethyl ammonium bromides were prepared by bubbling anhydrous HBr (Matheson) into chloroform solutions of the respective amines.

Chloroform (Fisher Spectral Grade) was purified of its ethanol preservative by extracting six times with distilled water and then drying over calcium hydride, followed by fractional distillation. An n.m.r. spectrum of the purified chloroform showed it to be completely free of ethanol. Benzene (Mallinkrodt) was first dried over sodium–lead alloy and then fractionally distilled. Tetramethylsilane (Anderson) was used without further purification.

Apparatus and Methods

Spectra were measured with a Varian HR-60 High Resolution NMR Spectrometer which has a fixed frequency of 60 Mc. Calibration was by means of 60 c.p.s. side bands on the tetramethylsilane peak. Each spectrum was scanned several times in each direction and average values of chemical shifts were taken relative to tetramethylsilane, the internal reference ($\delta = 0$ c.p.s.). Complexes were dissolved in purified chloroform or benzene such that concentrations were approximately 1 mole %.

ACKNOWLEDGMENTS

We thank Dr. A. Taurins and Dr. C. Stammer for the n.m.r. measurements and for helpful discussions. We are grateful to the Defence Research Board for financial assistance and to the National Research Council for the award of scholarships to one of us (J. M. M.). We are also grateful to a referee for several helpful comments.

REFERENCES

1. P. DIEHL and R. A. OGG. Nature, **180**, 1114 (1957).
2. P. DIEHL and J. GRANACHER. Helv. Phys. Acta, **31**, 43 (1958).
3. T. P. ONAK, H. LANDESMAN, R. E. WILLIAMS, and I. SHAPIRO. J. Phys. Chem. **63**, 1533 (1959).
4. W. D. PHILLIPS, H. C. MILLER, and E. L. MUETTERTIES. J. Am. Chem. Soc. **81**, 4496 (1959).
5. T. D. COYLE and F. G. A. STONE. J. Am. Chem. Soc. **83**, 4138 (1961).
6. O. OHASHI, Y. KURITA, T. TOTANI, H. WATANABE, T. NAKAGAWA, and M. KUBO. Bull. Chem. Soc. Japan, **35**, 1317 (1962).
7. R. A. CRAIG and R. E. RICHARDS. Trans. Faraday Soc. **59**, 1962 (1963).
8. R. R. HOLMES and R. P. CARTER, JR. Inorg. Chem. **2**, 1146 (1963).
9. H. C. BROWN and R. R. HOLMES. J. Am. Chem. Soc. **78**, 2173 (1956).
10. H. C. BROWN and L. DOMASH. J. Am. Chem. Soc. **78**, 5384 (1956).
11. C. M. BAX, A. R. KATRITZKY, and L. E. SUTTON. J. Chem. Soc. 1258 (1958).
12. M. F. LAPPERT. J. Chem. Soc. 542 (1962).
13. D. COOK. Can. J. Chem. **41**, 522 (1963).
14. J. M. MILLER and M. ONYSZCHUK. Can. J. Chem. **41**, 2898 (1963).
15. B. P. DAILEY and J. N. SCHOOLERY. J. Am. Chem. Soc. **77**, 3977 (1955).
16. A. A. BOTHNER-BY and C. NAAR-COLIN. J. Am. Chem. Soc. **80**, 1728 (1958).
17. F. A. COTTON and J. R. LETO. J. Chem. Phys. **30**, 993 (1959).
18. J. A. POPLE, W. G. SCHNEIDER, and H. J. BERNSTEIN. High resolution nuclear magnetic resonance. McGraw-Hill, New York. 1959. p. 101.
19. E. BULLOCK, D. G. TUCK, and E. J. WOODHOUSE. J. Chem. Phys. **38**, 2318 (1963).
20. J. T. EDWARD, A. TAURINS, and C. STAMMER. Private communication.