phosphine appears to be unique in that it is the only biphosphine to be shown to have both the *gauche* and *trans* structures in the liquid phase. It is difficult to give a reasonable explanation for this behavior since sterically chloride- and methyl-substituted compounds should be similar. It may be the "normal" behavior for the substituted biphosphines and we plan to determine the symmetries of several additional substituted biphosphines in the liquid state in order to find a possible trend in their behaviors. Recently Gimarc has been able to predict the structures of X_2Y_2 molecules by simple molecular orbital theory.[24] It would seem a similar study of X_2Y_4 molecules could also lead to reasonable explanations for the structures of this group of molecules.

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[24] B. M. Gimarc, private communication.

Notes

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Nuclear Magnetic Resonance Spectra of Several Trimethylamine–Boron Trihalide Complexes[1]

BY PATTY HALL CLIPPARD AND ROBERT COOPER TAYLOR

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Despite the continuing interest in Lewis acid–base complexes and the usefulness of nuclear magnetic resonance as a method of studying the molecular properties of these compounds, the number of nmr data available relating to typical donor–acceptor atoms are rather few. Little has been done in attempting to interpret results in terms of the electron distribution in the dative bond, a situation due, at least in part, to the scarcity of data. As part of another investigation, proton and boron-11 nmr spectra have been obtained for a number of trimethylamine adducts of boron halides and the results are reported here to corroborate and extend existing data.

At present, proton nmr spectra are available for trimethylamine complexes of BF_3, BCl_3, and BBr_3,[2-5] but no data have been published for the BI_3 complex. Since the literature results were obtained from samples prepared from natural boron, some ambiguity exists in the interpretation of the spectra due to complications introduced by the presence of two boron isotopes.

Boron-11 nmr spectra for these adducts have also been published[5-7] but, again, not on isotopically enriched compounds. Splittings due to coupling with nitrogen-14 have not been observed and no boron-11 spectra of nitrogen-15-enriched compounds have been reported. The B–N coupling constant is of some interest since it is directly related to the dative bond.

Experimental Section

Materials.—The complexes $(CH_3)_3N^{11}BX_3$ or $(CH_3)_3{}^{15}N^{11}BX_3$ were prepared by standard methods as described in ref 1. The fluoro, chloro, and bromo compounds were purified by sublimation and the iodo adduct was freshly crystallized from chloroform just before examination.

Apparatus and Method.—All spectra were taken at room temperature on a Varian HR-100 nuclear magnetic resonance spectrometer. The ^{11}B spectra were obtained using the instrument operating at 32.1 Mc with $B(CH_3)_3$ as the external standard. Calibration was by means of the known frequency separation of the side band and center band and the displacement of the center band from the external reference signal. The compounds were dissolved in $CDCl_3$ for the proton nmr studies and in acetone or acetonitrile for the boron-11. Chemical shifts in the proton spectra are estimated accurate to 0.002 ppm, and the coupling constants are estimated to 0.1 cps. In the boron-11 spectra, chemical shifts are estimated to 0.3 ppm and coupling constants are estimated to 1 cps.

Results and Discussion

Proton nmr spectra of boron-11-enriched $(CH_3)_3NBX_3$ complexes and also the boron-10-enriched chloro adduct are shown in Figure 1 and the chemical shifts and spin–spin coupling constants are listed in Table I. In $(CH_3)_3N^{11}BCl_3$, -$^{11}BBr_3$, and -$^{11}BI_3$, the methyl proton signal is split by the ^{11}B nucleus (spin $^3/_2$) into

TABLE I
PROTON CHEMICAL SHIFTS AND COUPLING CONSTANTS FOR SOME TRIMETHYLAMINE–BORON TRIHALIDE COMPLEXES

Compound	δ, ppm[a]	J_{BH}, cps
$(CH_3)_3N^{11}BF_3$[b]	-2.612	. . .
$(CH_3)_3N^{11}BCl_3$[b]	-3.005	2.6
$(CH_3)_3N^{11}BBr_3$[b]	-3.160	2.9
$(CH_3)_3NBI_3$[c]	-3.369	3.4
$(CH_3)_3N^{10}BCl_3$	-3.002	0.85

[a] Downfield from tetramethylsilane standard. [b] Chemical shift and coupling constant values obtained for these three compounds agree satisfactorily with values previously published.[2,3] [c] The boron-11 enriched adduct was impure and gave a more complex nmr spectrum than the compound prepared with natural BI_3.

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[1] Taken from a Ph.D. dissertation submitted by P. H. Clippard to the Horace H. Rackham School of Graduate Studies of The University of Michigan, Jan 1969.

[2] J. M. Miller and M. Onyszchuk, *Can. J. Chem.*, **42**, 1518 (1964).

[3] A. Derek, H. Clague, and A. Danti, *Spectrochim. Acta*, **23A**, 2359 (1967).

[4] O. Ohashi, Y. Kurita, T. Totani, H. Watanabe, T. Nakagawa, and M. Kubo, *Bull. Chem. Soc. Japan*, **35**, 1317 (1962).

[5] C. W. Heitsch, *Inorg. Chem.*, **4**, 1019 (1965).

[6] H. Noth and H. Vahrenkamp, *Chem. Ber.*, **99**, 1049 (1966).

[7] D. E. Young, G. E. McAchran, and S. G. Shore, *J. Am. Chem. Soc.*, **88**, 4390 (1966).

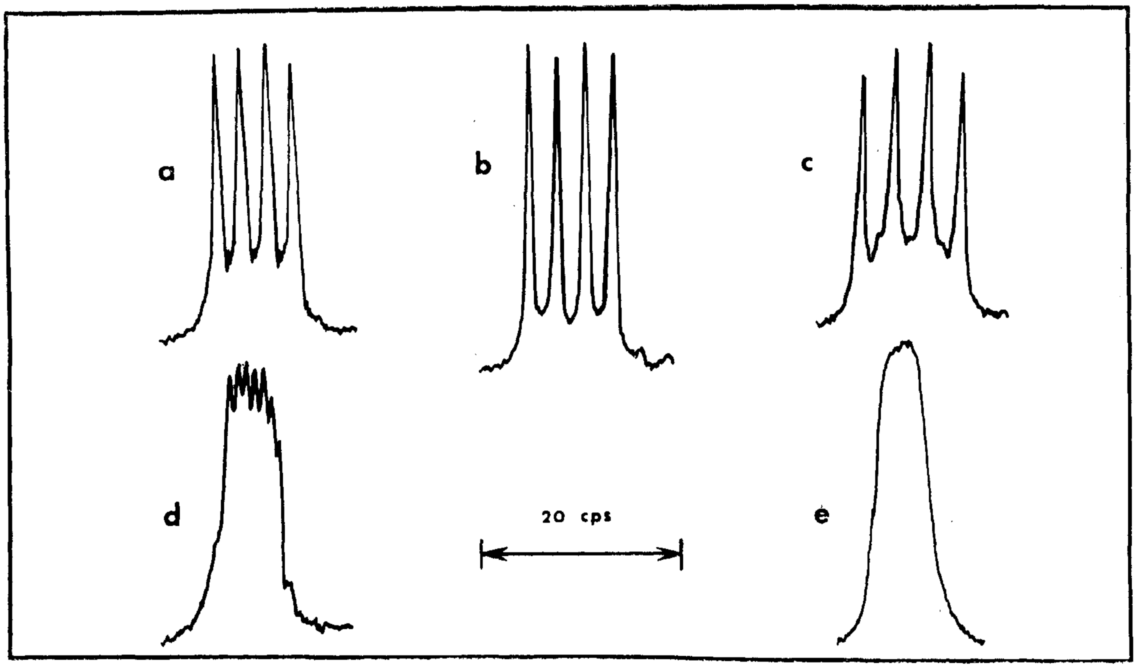

Figure 1.—Proton nmr spectra of (a) $(CH_3)_3N^{11}BCl_3$, (b) $(CH_3)_3N^{11}BBr_3$, (c) $(CH_3)_3NBI_3$, (d) $(CH_3)_3N^{10}BCl_3$, and (e) $(CH_3)_3N^{11}BF_3$, all in $CDCl_3$.

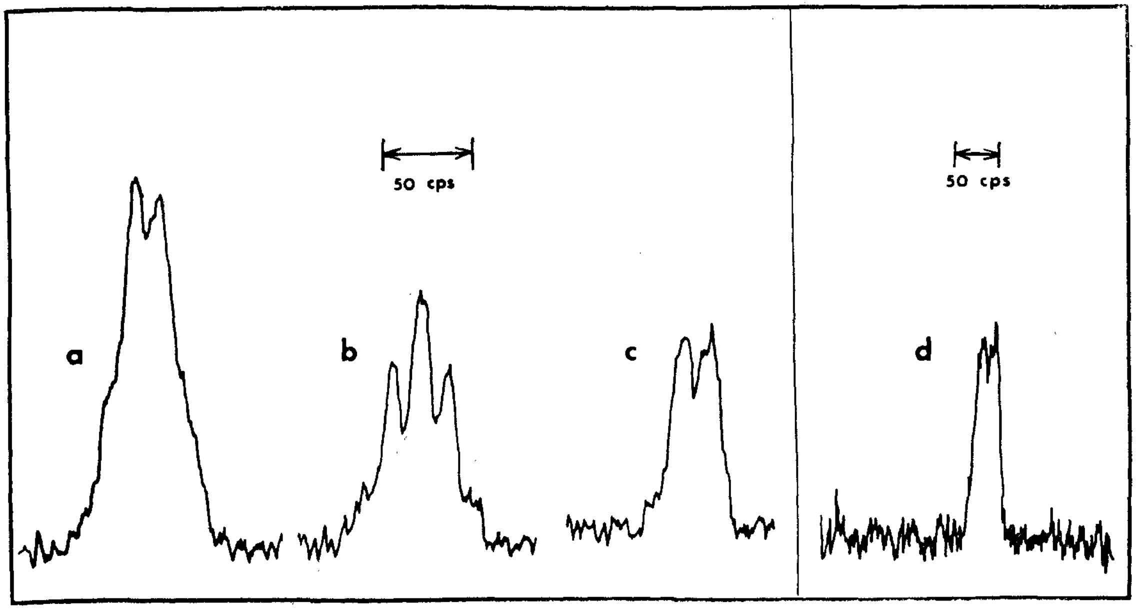

Figure 2.—Boron-11 nmr spectra of (a) $(CH_3)_3N^{11}BF_3$, (b) $(CH_2)_3{}^{15}N^{11}BF_3$, (c) $(CH_3)_3{}^{15}N^{11}BCl_3$, and (d) $(CH_3)_3{}^{15}N^{11}BBr_3$, all in acetone.

a 1:1:1:1 quartet. Miller and Onyszchuk[2] observed a further splitting of the quartet into pronounced doublets separated by about 0.7 cps. Such splitting was not observed in the present work nor in the investigations of Derek, Clague, and Danti[3] and Ohashi, *et al.*[4]

In the previous work based on the normal isotopic mixture of boron isotopes, the ^{10}B septet was superimposed on the more intense quartet from ^{11}B. Derek and coworkers assumed that the separations of peaks in the septet was approximately half that found in the quartet. However, the present work on complexes isotopically enriched in ^{10}B shows that the $^{10}B:^{11}B$ ratio of splittings (and hence the ratio of the coupling constants) is approximately $^1/_3$.[8,9]

The fluoro complex did not exhibit a quartet but rather a broad band with unresolved fine structure. Miller and Onyszchuk also observed only a single peak but Derek and coworkers obtained ten partially resolved peaks which they attributed to the result of B–H and F–H coupling. Heitsch[5] also observed ten peaks.

As can be seen in Table I, the downfield chemical shifts of the proton peaks are in the order $BI_3 > BBr_3 > BCl_3 > BF_3$. It is interesting that this order is the

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[8] The magnetogyric ratio $J_{^{11}B}/J_{^{10}B}$ is equal to 2.986.[9]

[9] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959.

same as the order of electron-accepting ability of these acids (acid strength) as established by other methods even though the protons are not directly adjacent to the dative bond. Carbon-13 chemical shifts might be even more informative regarding the effective electron density on the nitrogen atom. However, the boron chemical shifts to be discussed next do not exhibit such a simple trend.

The ^{11}B nmr spectra of boron-11-enriched BF_3, BCl_3, and BBr_3 complexes prepared from nitrogen-14 or nitrogen-15 are shown in Figure 2 and the chemical shifts and coupling constants are given in Table II. The chloro and bromo adducts prepared from nitrogen-14 exhibited the expected singlets but the spectrum of the fluoro compound showed partially resolved fine structure. Boron–fluorine coupling would result in a quartet with a 1:3:3:1 intensity pattern which is consistent with observation. Heitsch[5] also observed ^{11}B–F coupling but Shore and coworkers[7] reported only a single peak for this compound and Noth and Vahrenkamp[6] merely reported the chemical shift and did not reproduce their spectrum.

TABLE II
BORON-11 CHEMICAL SHIFTS AND COUPLING CONSTANTS FOR SOME TRIMETHYLAMINE–BORON TRIHALIDE COMPLEXES

Compound	δ, ppm[a]	J_{BN}, cps
$(CH_3)_3{}^{14}NBF_3$	+85.9[b]	. . .
$(CH_3)_3{}^{14}NBCl_3$	+76.5[b]	. . .
$(CH_3)_3{}^{14}NBBr_3$	+89.9[b]	. . .
$(CH_3)_3{}^{14}NBI_3$	(+140.4)[c]	. . .
$(CH_3)_3{}^{15}NBF_3$	+85.9	14–15
$(CH_3)_3{}^{15}NBCl_3$	+76.6	14
$(CH_3)_3{}^{15}NBBr_3$	+89.8	13

[a] Upfield from $B(CH_3)_3$. The solvents used were acetone and acetonitrile. When chloroform was used, the chemical shift was less by about 1 ppm. [b] These values agree with those from other investigations.[5-7] [c] Value from ref 6.

The boron-11 spectra of the chloro and bromo compounds prepared from nitrogen-15 exhibited doublets attributed to B–N coupling with ^{15}N (spin $^1/_2$), the peak separation being 13–15 cps. By way of comparison, the B–P coupling constants in the analogous trimethylphosphine–boron trihalide adducts[7] fall in the range of 165–170 cps. Some disparity is to be expected since trimethylphosphine is a much softer base than trimethylamine, but the magnitude of the difference suggests that there is a significant difference in the nature of the B–N and B–P bonds.

The nitrogen-15-enriched fluoro complex exhibited a quintet which can be interpreted as the resultant of ^{19}F–^{11}B and ^{15}N–^{11}B couplings if the two coupling constants are about equal. Each member of the doublet produced by the ^{15}N would be split further into a 1:3:3:1 quartet by interaction with fluorine, the overlapping quartets producing a 1:4:6:4:1 quintet.

Inspection of the data in Table II shows an upfield increase in the chemical shifts from the chloro through the iodo compounds. However, the trend is not uniform and the position of the fluoro complex is not in the regular sequence. If the difference between the chemical shift of the adduct and that of the free BX_3 is considered,[10] the data fall in the correct order and show a more regular increase from fluoro to iodo compounds consistent with the order of acid strengths and also with the proton chemical shifts of the methyl groups. However, it is not clear whether this empirical observation has any particular significance.

Acknowledgment.—The authors are indebted to Mr. Frank Parker for obtaining the nmr spectra. This work was supported by the National Institutes of Health under Grant CA-07989. P. H. C. is indebted to the H. H. Rackham School of Graduate Studies of The University of Michigan for a fellowship.

(10) P. N. Gates, E. J. McLauchlan, and E. F. Mooney, *Spectrochim. Acta*, **21**, 1445 (1965).

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Boron Heterocycles. VI. A Mass Spectrometric Investigation of Selected Heteronuclear Diborane(4) Ring Systems[1]

BY G. L. BRUBAKER AND S. G. SHORE

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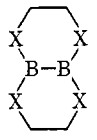
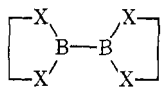
In the preceding article[1] of this series, the preparation and characterization of a number of heteronuclear diborane(4) ring compounds were discussed. Heterocyclic systems of composition $B_2(X_2C_2H_4)_2$ posed a problem of structure in that frameworks could be fused cyclic I or bicyclic II.



I, X = O,S



II, X = NCH_3

While techniques such as nmr and vibrational spectroscopy were of little use in assigning a structure to each compound, indirect chemical evidence was consistent with structure I when X = O or S and structure II when X = NCH_3.

In principle, mass spectrometry could be of use in distinguishing between the fused cyclic and bicyclic isomers. Therefore, the present study has been concerned with a mass spectral investigation of the heterocycles listed above and their acyclic analogs $B_2[N(CH_3)_2]_4$, $B_2(OCH_3)_4$, and $B_2(SCH_3)_4$ in the hope of relating fragmentation patterns to structures of parent species.

Results and Discussion

In order to use mass spectrometry as a structural tool, it was desirable to determine if symmetrical acyclic diborane(4) compounds which contain N, O, or S as substituent atoms produce a strong peak at *m/e* representing cleavage of the boron–boron bond to give

(1) Part V: C. N. Welch and S. G. Shore, *Inorg. Chem.*, **7**, 225 (1968).