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 | $\delta$, 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.

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

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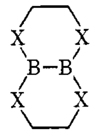
# Boron Heterocycles. VI. A Mass Spectrometric Investigation of Selected Heteronuclear Diborane(4) Ring Systems[1]

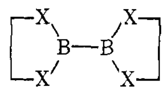
BY G. L. BRUBAKER AND S. G. SHORE

*Received March 24, 1969*

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. 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 = $NCH_3$.



I, X = O,S



II, 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

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

TABLE I

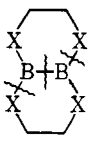
EXACT PARENT AND HALF-MASSES

| Compound | Mol wt (theory) | m/e (found) | 1/2 mol wt (theory) | m/e (found) | Rel intens | m/e (rel intens > 90%) |
|---|---|---|---|---|---|---|
| | | | Acycles | | | |
| $B_2[N(CH_3)_2]_4$ | 198.218710 | 198.218419 | 99.109355 | 99.10924 | 100 | 99 (100) |
| $B_2(OCH_3)_4$ | 146.092170 | 146.089491 | 73.046085 | 73.046056 | 97.6 | 31 (100), 73 (97.6) |
| $B_2(SCH_3)_4$ | 210.000806 | 210.157948 | 105.000403 | 105.000970 | 5.9 | 102 (100) |
| | | | Heterocycles | | | |
| $B_2[N_2(CH_3)_2C_2H_4]_2$ transamination | 194.187410 | 194.189236 | 97.093705 | 97.094337 | 19.2 | 193 (100), 194 (95.5) |
| $B_2[N_2(CH_3)_2C_2H_4]_2$ coupling | 194.187410 | 194.189664 | 97.093705 | 97.093992 | 19.2 | 193 (100), 194 (95.5) |
| $B_2(O_2C_2H_4)_2$ | 142.060870 | 142.073454 | 71.030435 | 71.031258 | 20.7 | 89 (100), 115 (99.3) |
| $B_2(S_2C_2H_4)_2$ | 205.969506 | 205.968823 | 102.984753 | 102.987066 | 16.1 | 178 (100) |

$BX_2^+$ ($X = N(CH_3)_2$, $OCH_3$, $SCH_3$), in the mass spectral cracking pattern. To this end, the mass spectra of three acyclic diborane(4) compounds were studied. Fragments from $B_2[N(CH_3)_2]_4$ and $B_2(OCH_3)_4$ which correspond to $B[N(CH_3)_2]_2^+$ and $B(OCH_3)_2^+$ were found to have relative intensities of 100 and 97.6%. In the case of $B_2(SCH_3)_4$, the fragment corresponding to $B(SCH_3)_2^+$ had a relative intensity of only 5.9%; however, a peak of relative intensity 100% was observed three units below the m/e of $B(SCH_3)_2^+$ thus suggesting that in this case, also, a principal fragment arises from symmetrical cleavage of $B_2(SCH_3)_4$.[2,3]

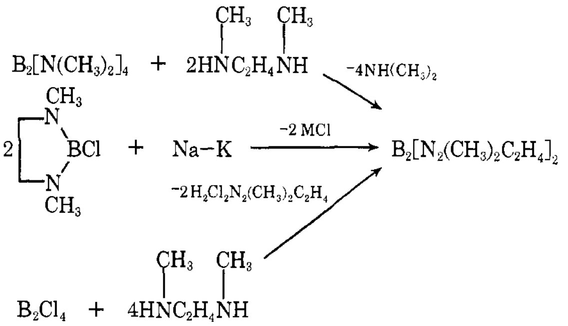
Mass spectral cracking patterns of the heterocyclic diborane(4) compounds were determined.[4] Salient features of the spectra are considered below.

The mass spectrum of each heterocycle studied is more easily interpreted in terms of a fused-ring structure, I, rather than a bicyclic structure, II. If the structures were bicyclic, the spectra would be expected to parallel those of the acyclic analogs. Principal fragmentation would be expected to occur at the boron–boron bond giving peaks of high intensity at mass to charge ratios at or just below half the mass of the parent molecule ion. On the other hand, the fused-ring structure would have to have three framework bonds broken in the fragmentation process in order to form a fragment corresponding to half the parent mass, *e.g.*



On the basis of statistical and energetic considerations, it seems reasonable to assume that the mass spectra of such structures would be unlike those of their acyclic analogs at *m/e*'s corresponding to the half parent mass region. In this region the intensities of the fragments would be expected to be relatively low for the heterocycles. Significant features of the mass spectral fragmentation data are presented in Table I and are consistent with this latter statement. From the data in the last column, it is seen that for the acyclic structures the highest intensities are observed at *m/e*'s of half or below half the mass of the parent molecule ion. On the other hand, for the heterocycles, the most intense peaks occur at mass to charge ratios greater than half the values for the parent mass, suggesting that the boron framework is held together by more than a single boron–boron bond.

The mass spectral data thus lend credence to the earlier chemical study which suggested that $B_2(O_2C_2H_4)_2$ and $B_2(S_2C_2H_4)_2$ are fused cyclic structures[1] but contradict the earlier representation of $B_2[N_2(CH_3)_2C_2H_4]_2$ as a bicycle.[5] This compound has been prepared in the following ways[1,5]



X-Ray powder diffraction patterns[1] and the mass spectra of this compound prepared by transamination and by coupling with Na–K alloy are identical. The principal argument for $B_2[N_2(CH_3)_2C_2H_4]_2$ being bicyclic has been based upon the fact that it can be

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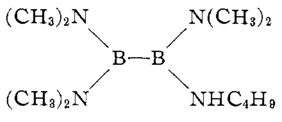
(2) A doubly charged parent molecule ion $B_2X_4^{2+}$ has the same *m/e* as the fragment of symmetrical cleavage, $BX_2^+$, and therefore contributes to its relative intensity. However, the available evidence suggests that the contribution is small since the intensities of other doubly charged species in the spectra of all of the molecules examined are relatively low. Furthermore, for the unsymmetrical acyclic diborane(4)



which has a parent mass of 226, the intensity of the peak which represents the doubly charged parent molecule ion (*m/e* 113) is small compared to intense peaks (*m/e* 99, 127) which correspond to the fragments produced upon cleaving the boron–boron bond.[3]

(3) R. W. Nelson, Doctoral Dissertation, Duke University, 1968.

(4) For complete fragmentation data, order Document No. NAPS-00585 from ASIS National Auxiliary Publications Service, c/o CCM Information Corp., 909 3rd Ave New York, N. Y. 10022, remitting $1.00 for microfiche or $3.00 for photocopies. Advance payment is required. Make check payable to: ASIS–NAPS.

(5) R. J. Brotherton, A. L. McClosky, L. L. Petterson, and H. Steinberg, *J. Am. Chem. Soc.*, **82**, 6242 (1960); M. P. Brown, A. E. Dann, D. W. Hunt, and H. B. Silver, *J. Chem. Soc.*, 4648 (1962).

prepared by means of a coupling reaction which generates a boron–boron bond. In a system of this sort, in which ternary boron is in the presence of potential nucleophiles such as nitrogen and chlorine in unreacted chloroborane, structural rearrangement to the fused cyclic ring system can be envisioned through a four-center mechanism.

### Experimental Section

**Mass Spectra.**—An Associated Electrical Industries MS-902 mass spectrometer operating at 70 eV was used to obtain mass spectra. Solid samples were introduced *via* a direct insertion probe. A heated inlet system was employed for liquid samples. Heptacosafluorotributylamine was used as a standard in exact mass determinations.

**Materials.**—All samples were handled by conventional vacuum line and drybox techniques. A complementary sample of $B_2[N(CH_3)_2]_4$ was obtained from U. S. Borax Research Corp. The compounds $B_2(OCH_3)_4$, $B_2(O_2C_2H_4)_2$, $B_2(S_2C_2H_4)_2$, and $B_2[N_2(CH_3)_2C_2H_4]_2$ were prepared using methods described previously in the literature.[1,5]

**$B_2(SCH_3)_4$.**—In a typical experiment, 6.88 mmol of $B_2[N(CH_3)_2]_4$ was dissolved in 40 ml of $CH_2Cl_2$ in a 100-ml bulb. Slight excesses (28.00 mmol) each of $CH_3SH$ and HCl were added to the solution at $-95°$. The bulb was allowed to warm to room temperature over a 4-hr period and stirred continuously for 12 hr. The solvent was removed by fractional distillation at $-45°$. $B_2(SCH_3)_4$, bp 115° (1–2 mm), a clear colorless liquid, was distilled from the reaction bulb leaving behind a crystalline white solid identified as $(CH_3)_2NH_2Cl$ by its X-ray powder pattern; yield, 95% based upon the amount of salt recovered.

**Acknowledgment.**—We wish to acknowledge, gratefully, the support of this work by the National Science Foundation.

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## The Infrared and Raman Vibrational Spectra and Structure of Potassium *sym-trans-μ*-Ethyleno-bis(pentacyanocobaltate(III))

BY W. A. MCALLISTER AND L. T. FARIAS

*Received June 5, 1969*

In a continuation of our spectroscopic studies on coordination compounds and specifically on compounds with bridging ligands,[1] we have investigated the infrared and Raman spectra of potassium *sym-trans-μ*-ethylenobis(pentacyanocobaltate(III)). Its resemblance to one possible structure of the "red" isomer of the pentaminenitrosylcobalt ion is obvious. One difficulty encountered with the latter compound was the assignment of a possibly symmetrical N–N stretching frequency to a rather strong infrared band. If this ion did contain a *sym-trans-μ*-hyponitrito linkage, this band would be expected to be infrared forbidden. It has so far been impossible to carry out a Raman study using the present laser source, which causes decomposition. It was hoped that through the present study further information could also be obtained involving the structural assignment of the "red" isomer.

The dipentacyanocobalt–ethylene complex could have either the *cis* or *trans* structure. Using steric considerations the *cis* isomer seems unlikely as pointed out in its initial investigation.[2] However, a strong band at 1622 $cm^{-1}$ was assigned to the C–C stretching mode. Through a complete vibrational analysis involving deuterium-substituted species, we hoped to establish the configuration of this complex.

### Experimental Section

Potassium *sym-trans-μ*-ethyleno-bis(pentacyanocobaltate(III)) was prepared as reported by Griffith and Wilkinson.[2] We were also able to prepare the identical compound through the reaction of acetylene and the hydridopentacyanocobalt(II) ion.[3] The deuterated compound was prepared by carrying out the preparation in $D_2O$ carefully excluding all $H_2O$. It was hoped that the compound could be prepared with the four waters of crystallization as $D_2O$ and separately with the deuterated ethylenic linkage, but due to exchange this was impossible. The entire system was deuterated using $C_2D_2$ prepared from calcium carbide and $D_2O$.

The Raman spectra were recorded on a Cary Model 81 spectrophotometer equipped with a 6328-Å He–Ne laser source. Samples were run only as solids, because the solutions decomposed in the laser beam. The infrared spectra were recorded from 4000 to 200 $cm^{-1}$ using a Beckman IR-12 spectrophotometer with the calibration checked in the usual manner.[4,5] Samples were examined as Nujol mulls on KBr plates as well as in KBr and CsI disks. The very far-infrared spectra were recorded on a Beckman IR-11 utilizing samples prepared as Nujol mulls supported between polyethylene plates. Both instruments were purged with dry air. Sharp bands are expected to be within $\pm 2\ cm^{-1}$.

Analyses for the compound were performed by Galbraith Laboratories, Knoxville, Tenn. *Anal.* Calcd for $K_6[Co(CN)_5]_2C_2H_2 \cdot 4H_2O$: C, 20.3; H, 1.7; N, 19.7. Found: C, 19.0; H, 1.7; N, 20.0. There was no sign of decomposition during the recording of the spectrum. A check was also made for strong bands from $K_3[CO(CN)_6]$.

### Results and Discussion

The infrared and Raman spectra of $K_6[Co(CN)_5]_2C_2H_2 \cdot 4H_2O$ and $K_6[Co(CN)_5]_2C_2D_2 \cdot 4D_2O$ were recorded from 4000 to 50 $cm^{-1}$. This compound is expected from steric considerations to have $C_{2h}$ symmetry about the ethylene linkage and $C_{4v}$ symmetry about each cobalt atom. From the infrared and Raman studies on this compound and its deuterated analog, it was possible unequivocally to confirm these expectations.

**Infrared and Raman Spectral Assignment.**—In order to simplify the band assignments, they will be divided into those associated with the *trans*-ethylenic linkage followed by those from the metal and its coordinated atoms.

Assignments for the fundamental frequencies in the ethylenic linkage are presented in Table I. These assignments are in excellent agreement with the absorption bands previously reported for the *trans*-dihalo-

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[1] E. E. Mercer, W. A. McAllister, and J. R. Durig, *Inorg. Chem.*, **6**, 1816 (1967).

[2] W. P. Griffith and G. Wilkinson, *J. Chem. Soc.*, 1629 (1959).

[3] N. K. King and M. E. Winfield, *J. Am. Chem. Soc.*, **83**, 3366 (1961).

[4] "Tables of Wavenumbers for the Calibration of Infrared Spectrometers," IUPAC, Butterworth Inc., Washington, D. C., 1961.

[5] H. M. Randall, D. M. Dennison, N. Ginsberg, and L. R. Weber, *Phys. Rev.*, **52**, 160 (1947).