BORON–NITROGEN COMPOUNDS

XXII*. THE INFRARED SPECTRUM OF BIS(DIMETHYLAMINO)METHYL-BORANE**

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The reactions of bisaminoboranes, $R'B(NR_2)_2$ (I), have recently been studied in some detail. For example, condensation of bisaminochloroboranes (I, $R' = Cl$) with alkali metals[2,3] has provided ready access to diborane(4) derivatives, $(R_2N)_2B–B(NR_2)_2$, and the transamination of bisaminoboranes with α,ω-diamines was found to be a facile method for the preparation of boron–nitrogen–carbon heterocycles[4]. However, relatively little information is available on the physicochemical properties of bisaminoboranes.

Previously, the infrared spectra of several bis(monoalkylamino)phenylboranes, $C_6H_5B(NHR)_2$, have been reported by Burch *et al.*[5]. The infrared spectrum of bis-(dimethylamino)methylborane (I, $R = R' = CH_3$) is reported in the following study. The major vibrations of the compound were assigned by considering band intensities and band shapes as well as isotope effects. On this basis, reasonably certain assignments can be made.

BIS(DIMETHYLAMINO)METHYLBORANE

The infrared spectra of bis(dimethylamino)(trideuteromethyl)borane and of bis(dimethylamino)methylborane with the natural abundance of boron isotopes and of a ^{10}B-enriched sample (92 % ^{10}B) in the range 700–4000 cm^{-1} are listed in Table 1.

The observed frequencies as shown in Table 1 permit assignment of the antisymmetric and symmetric BN_2 stretching vibrations of bis(dimethylamino)methylborane as one of the most interesting features of the spectra. The extremely high absorption of $\nu_{as}(BN_2)$ at 1502 cm^{-1} might well reflect a high degree of BN bond order in the molecule. However, the concept of relating a BN frequency directly to the bond order (*i.e.* the valence force constant) has two major weaknesses: It disregards mass effects of the substituents on the boron and the nitrogen atoms and also reciprocal coupling of the various vibrations. In addition, the electronic nature of the substituents may directly influence the bond order.

In a series of related compounds, mass effects of the substituents appear to be of minor importance. For example, in a number of trialkylboranes, BR_3, the BC stretch has been consistently found in the range of 1120–1135 cm^{-1}, the only exception

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* For Part XXI see ref. 1.
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TABLE 1

INFRARED SPECTRA OF BIS(DIMETHYLAMINO)TRIDEUTEROMETHYLBORANE (A), BIS(DIMETHYL-AMINO)METHYLBORANE (B) AND ^{10}B-ENRICHED BIS(DIMETHYLAMINO)METHYLBORANE (C)

Frequencies in cm^{-1}.

w = weak; m = medium; s = strong; v = very; x = extremely; b = broad; sh = shoulder.

A	B	C	Assignments
771 vs			
790 m			$\rho(CD_3)$
841 w			
873 vw			
	878 m		$\nu(BCH_3)$
	891 sh w	890 m	
914 s			
923 sh m			$\nu(BCD_3)$
933 sh w			
	949 s	952 s	$\rho(CH_3)$
		973 vw	
1010 sh w			
1023 sh m			$\delta_s(CD_3)$
1063 vs	1063 vs	1067 s	$\nu_s(NC_2)$
1103 sh w	1111 w	1108 sh w	
1127 xs (b)	1130 vvs (b)	1128 sh m	$\rho(CH_3) + \delta_{as}(CD_3)$
1140 sh vs (b)	1143 vs (b)	1135 s (b)	$\rho(CH_3)$
1152 sh s	1151 sh s	1152 vs	
1192 vs-s	1194 vs	1196 s	$\nu_{as}(NC_2)$
1225 vs	1219 vs	1225 vs	$\rho(CH_3)$
		1286 vw	
	1300 s	1302 m-s	$\delta_s(B)CH_3$
		1330 sh w	
1362 sh vs	1364 sh vs	1366 sh s	
1378 xs	1376 xs		$\nu_s(BN_2)$
1390 sh vs	1392 sh vs	1398 xs	
1408 vs	1409 s-vs	1414 vs-s	
1449 vs	1452 sh vs	1456 vs	$\delta(CH_3)$
1468 sh s	1469 sh vs	1468 vs	
1502 xs	1502 xs	1500 sh vs	$\nu_{as}(BN_2)$
1521 sh vs	1521 sh vs	1520 xs	
1980 w			
2180 m			νCD
2210 m-s			
2460 w			
2778 s			
	2796 s	2808 s	
2830 vs	2840 vs	2863 vs	νCH
2967 s	2972 s	2924 sh s	
		3002 s	

being trimethylborane ($\nu BC = 1165$ cm^{-1})[6,7]. Similarly, we did not observe any appreciable changes in the position of $\nu_{as}(BN_2)$ by replacing the boron substituent $R = CH_3$ in $RB[N(CH_3)_2]_2$ by $R = CD_3$, C_2H_5 or n-C_4H_9. Also, within the series $CH_3B(NR_2)_2$ where $R = CH_3$, C_2H_5 or n-C_3H_7 the antisymmetric BN stretching frequency appears to be quite independent of the chain length of R and therefore of the mass of the substituents at the nitrogen atoms; $\nu_{as}(BN_2)$ of the cited compounds was consistently observed near 1500 cm^{-1}. This observation is substantiated by the findings of Burch et al.[5], who reported similar results for bis(monoalkylamino)phenylboranes.

Several years ago, Becher[8] demonstrated that N-phenylation decreases the BN frequency in organic substituted monoaminoboranes, $R_2B–NR'_2$. He concluded that the frequency decrease corresponds to a decrease of the force constant k_{BN} and hence the BN bond order. On the other hand, replacement of a B-alkyl group by phenyl hardly affects the BN frequency of a monoaminoborane[9,10]. These observations have been interpreted in terms of electronic interactions of the π-electrons of the benzene ring with the adjacent atoms[9,10] and the experimental data were found to be in good agreement with molecular orbital calculations[11]. However, an increase in the BN frequency does not necessarily reflect an increase in the BN bond order or *vice versa*. More recently, Becher[12] has studied some methylated monoaminoboranes and was able to demonstrate that a correlation of valence vibrations (even of BN multiple bonds) with the bond order requires a detailed consideration of the coupling of vibrations. In order to deduce this information accurately, it is necessary not only to obtain reliable assignments for the majority of absorptions of a given molecule, but also to have a sufficient number of compounds for comparative purposes at hand in order to evaluate the actual trend of frequency shifts. For example, Becher[12] reports the trend of the three symmetrical vibrations $\nu(BN)$, $\nu_s(NR_2)$ and $\delta(NR_2)$ for the compounds $(CH_3)_2B–NH_2$, $(CH_3)_2B–ND_2$ and $(CH_3)_2B–N(CH_3)_2$ as illustrated in Table 2. If the three vibrations of each compound are considered as a complete system, a frequency decrease is apparent. On the other hand, if that vibration alone is selected in which the potential energy of the BN bond is most eminent, its frequency increases in relation to the position of the coupling vibration.

In the present study most of the assignments in Table I appear to be justified. The frequency shift $\nu(CH)–\nu(CD)$ as observed for the boron-attached methyl group in bis(dimethylamino)methylborane is in agreement with the reported values of $\nu(CH)$ and $\nu(CD)$ for the transition $B(CH_3)_3 \rightarrow B(CD_3)_3$[7]. Furthermore, it is known that the symmetrical deformation vibration $\delta_s(CH_3)$ is altered when a methyl group is attached to an element other than carbon, in which case the electronegativity of that element becomes an important factor. In Table 3 expected frequencies of $\delta_s(CH_3)$, reflecting their dependence on the adjacent atom, are listed. These data substantiate the corresponding assignments of Table I.

TABLE 2

FREQUENCY TRENDS IN METHYLATED MONO-AMINOBORANES
Frequencies in cm^{-1}.

	$\nu(BN)$	$\nu_s(NR_2)$	$\delta(NR_2)$
$(CH_3)_2B–NH_2$	1447	3450	1615
$(CH_3)_2B–ND_2$	1470	2500	1145
$(CH_3)_2B–N(CH_3)_2$	1525	983	431

TABLE 3

THE $\delta_s(CH_3)$ FREQUENCY IN DEPENDENCE OF THE ADJACENT ATOM

Adjacent atom	$\delta_s(CH_3)$ (cm^{-1})
N	$\sim$ 1420
C	$\sim$ 1380
^{10}B	$\sim$ 1310
^{11}B*	$\sim$ 1300

* $\delta_s(B)CD_3 \sim$ 1020 cm^{-1}.

The antisymmetric and symmetric NC_2 stretching modes of bis(dimethylamino)-methylborane were assigned in analogy to the corresponding assignments of tris(di-methylamino)borane[13]. Therefore the assignment of the BC stretch in Table I seems to

be the major remaining factor of uncertainty. However, the known spectroscopic data of isotopically labeled trimethylborane and of a number of bisaminoborane systems as illustrated in Table 4 make the assignments of Table 1 appear reasonable.

TABLE 4

THE POSITION OF ν(BC) IN SOME METHYLBORANES
Frequencies in cm^{-1}.

Compound	ν(BC)	Reference
B(CH$_3$)$_3$	1156	6
^{10}B(CH$_3$)$_3$	1178	6
B(CD$_3$)$_3$	1205	6
CH$_3$B(NH)$_2$(CH$_2$)$_2$	858	17
CH$_3$B(NH)$_2$(CH$_2$)$_3$	887	18
CH$_3$^{10}B(NH)$_2$(CH$_2$)$_3$	898	18
CD$_3$B(NH)$_2$(CH$_2$)$_3$	931	18
CH$_3$B(NH)$_2$(CH$_2$)$_4$	838	18

BIS(DIMETHYLAMINO)BORANE AND BIS(DIMETHYLAMINO)CHLOROBORANE

In order to deduce other useful information from the spectral data of bis(dimethylamino)methylborane, the coupling of vibrations must be considered briefly. Therefore, the infrared spectra of bis(dimethylamino)borane, HB[N(CH$_3$)$_2$]$_2$, and of bis(dimethylamino)chloroborane, ClB[N(CH$_3$)$_2$]$_2$, were recorded. The data obtained in the range of 700–1600 cm^{-1} are listed in Table 5. Assignments of the frequencies of present interest were made in consonance with the foregoing considerations.

In comparison with the materials listed in Table 1, no changes were made at the nitrogen sites of the B(NR$_2$)$_2$ part of the molecule. As noted above, mass effects of the substituents at least appear to be negligible. If then the BN frequency could be considered proportional to the BN valence force constant, this relationship would indicate an extraordinary high BN bond order for bis(dimethylamino)borane. Alternatively, the BN vibration is influenced by either the electronic nature of the boron substituent, in this case hydrogen, or the BN frequency reflects coupling of this mode with BH vibrations. It is, therefore, of interest to note that the BH stretch of bis-(dimethylamino)borane was recorded near 2450 cm^{-1}. This value is at the lower end of the frequency region normally associated with the BH stretching vibration of a single terminal BH group (2450–2565 cm^{-1}). In contrast, the BCl valence vibration of bis(dimethylamino)chloroborane was observed at an unusual high frequency when compared to the values reported for (dialkylamino)chloroboranes, R$_2$N–BHCl [ν(BCl) = 770–790 cm^{-1}][14]. Therefore, in the two bis(dimethylamino)boranes under consideration, coupling of vibrational modes of the boron substituents with the BN

vibration seems apparent. Nevertheless, even considering coupling effects, the observed BN frequencies seem to indicate a relatively high BN bond order.

TABLE 5

INFRARED SPECTRA OF BIS(DIMETHYLAMINO)BORANE (D) AND BIS(DIMETHYLAMINO)CHLOROBORANE (E)

Frequencies in cm^{-1}.

w = weak; m = medium; s = strong; v = very; sh = shoulder.

D	E	Assignments
810 w		
862 s		
878 s		
	898 vs	} ν(BCl)
	918 w	
962 m	958 vw	
1058 vs	1064 vs	ν_s(NC$_2$)
1080 s–vs		
1142 s	{1138 vs	ρ(CH$_3$)
	{1146 sh s	
{1163 s–vs		δ(BH)
{1189 m–w	1188 s	ν_{as}(NC$_2$)
	1210	
1225 vs		
1237 vs		
1354 s	1353 vs	δ(CH$_3$)
{1398 vvs	{1400 vvs	} ν_s(BN$_2$) + δ(CH$_3$)
{1409 sh vs	{1414 sh vvs	
1455 vs	{1455 vs	δ(CH$_3$)
{1462 vs	{1466 sh s	δ(CH$_3$)
{1485 sh s	1490 w	
{1530 vvs	{1530 vvs	} ν_{as}(BN$_2$)
{1548 sh vvs	{1547 sh vvs	

RESULTS

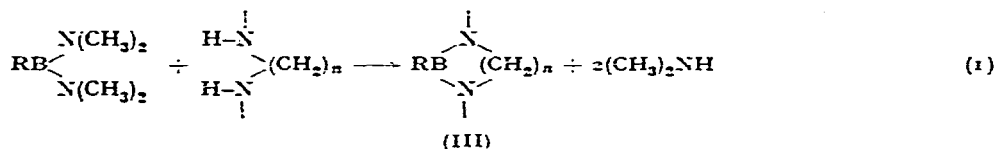On comparing the data of Tables 1 and 5, the rather constant position of ν_{as}(NC$_2$) near 1190 cm^{-1} and ν_s(NC$_2$) near 1060 cm^{-1} in all five derivatives is remarkable. This observation might suggest relatively little coupling of the NC modes with the vibrations associated with the boron atom. The free electron pair of the nitrogen superimposes $p_\pi–p_\pi$ bonding on the BN σ bond. This event requires planarity or near planarity of the BN bonds and, therefore, part (II) of the bis(dimethylamino)methylborane molecule should be planar. Examination of molecular models shows this

$$-\overset{\displaystyle |}{N}\diagdown_{\diagdown B\diagup}\overset{\displaystyle |}{N}-$$
$$\underset{\displaystyle CH_3}{\overset{\displaystyle |}{}}$$

(II)
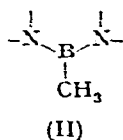
structure to be quite feasible. As a matter of fact, even the NC$_2$ groups may be planar with the rest of the molecule, although a state of completely unhindered rotation of the N-attached methyl groups may require a slight distortion of the NC$_2$ groups

out of the BN_2 plane. This basic situation does not change on replacement of the *B*-methyl group by either hydrogen or chlorine, since the latter atoms will not sterically interfere with the rest of the molecule.

The foregoing discussion then suggests the conclusion that ring closure of a bisaminoborane in a transamination reaction as illustrated in equation (1) should not drastically affect vibrational modes associated with the boron atom, provided that no ring strain occurs. If in eqn. (1) $n = 3$, the resultant product (III) will be a member

$$RB \begin{matrix} N(CH_3)_2 \\ \\ N(CH_3)_2 \end{matrix} + \begin{matrix} H-N \\ \\ H-N \end{matrix} (CH_2)_n \longrightarrow RB \begin{matrix} N \\ (CH_2)_n \\ N \end{matrix} + 2(CH_3)_2NH \qquad (1)$$

(III)

of a ring system with six annular atoms. The latter are known to be virtually free of ring strain and therefore the 1,3,2-diazaboracyclohexane system (III, n = 3) should have many spectral features comparable to acyclic bisaminoboranes. Certainly in (III), $p_\pi - p_\pi$ overlap is possible and therefore the RBN_2 part of the molecule is expected to be planar: in addition, the $(CH_2)_3$ part of the molecule should compare favorably with the corresponding arrangement in cyclohexane. Therefore, the present data may serve as a basis for the evaluation of the spectra of 1,3,2-diazaboracycloalkanes. This conclusion is important since BN heterocycles comprise a particularly suitable structure for studying the nature of the BN bond.

EXPERIMENTAL

Preparation of materials

Tris(dimethylamino)borane was disproportionated with trichloroborane to yield bis(dimethylamino)chloroborane. Subsequent reaction of this product with CH_3MgI, CD_3MgI or LiH proceeds smoothly to yield the desired materials[14,15]. The [10]B-enriched derivatives were obtained in like manner by synthesizing [10]B-trichloroborane from commercially available, isotopically enriched boric acid by the reaction of aluminum trichloride with $B(OC_6H_5)_3$[16].

Recording of spectra

The purity of the materials was controlled by ^{1}H nuclear magnetic resonance spectroscopy and by vapor phase chromatography. All spectra were recorded from films of the liquid compounds using a Perkin–Elmer Model 21 double beam spectrophotometer having sodium chloride optics.

SUMMARY

Major infrared absorptions of bis(dimethylamino)methylborane were assigned on the basis of studies with isotopically labeled materials. The influence of substituents on the BN stretching vibration is discussed and factors concerning the elucidation of the BN bond nature in the bisaminoborane system from spectral data are evaluated.

REFERENCES

1 Part XXI: K. NIEDENZU, J. W. DAWSON AND P. FRITZ, *Z. Anorg. Allgem. Chem.*, in press.
2 R. J. BROTHERTON, A. L. MCCLOSKEY, L. L. PETTERSON AND H. STEINBERG, *J. Am. Chem. Soc.*, 82 (1960) 6242.
3 H. NÖTH AND W. MEISTER, *Chem. Ber.*, 94 (1961) 509.
4 K. NIEDENZU, P. FRITZ AND J. W. DAWSON, *Inorg. Chem.*, 3 (1964) 1077.
5 J. E. BURCH, W. GERRARD, M. GOLDSTEIN, E. F. MOONEY AND H. A. WILLIS, *Spectrochim. Acta*, 18 (1962) 1403.
6 W. J. LEHMANN, C. O. WILSON, JR., AND I. SHAPIRO, *J. Chem. Phys.*, 28 (1958) 777.
7 W. J. LEHMANN, C. O. WILSON, JR., AND I. SHAPIRO, *J. Chem. Phys.*, 31 (1959) 1071.
8 H. J. BECHER, *Z. Anorg. Allgem. Chem.*, 289 (1957) 262.
9 G. M. WYMAN, K. NIEDENZU AND J. W. DAWSON, *J. Chem. Soc.*, (1962) 4068.
10 H. T. BAECHLE AND H. J. BECHER, *Spectrochim. Acta*, 21 (1965) 579.
11 J. J. KAUFMAN AND J. R. HAMANN, *Advances in Chemistry Series*, Vol. 42, American Chemical Society, Washington D.C., 1964, p. 95.
12 H. J. BECHER, *Spectrochim. Acta*, 19 (1963) 575.
13 H. J. BECHER, *Z. Anorg. Allgem. Chem.*, 287 (1956) 285.
14 H. NÖTH, W. A. DOROCHOV, P. FRITZ AND F. PFAB, *Z. Anorg. Allgem. Chem.*, 318 (1962) 293.
15 H. NÖTH AND P. FRITZ, *Z. Anorg. Allgem. Chem.*, 322 (1963) 297.
16 H. J. BECHER, personal communication.
17 J. GOUBEAU AND A. ZAPPEL, *Z. Anorg. Allgem. Chem.*, 279 (1955) 38.
18 K. NIEDENZU *et al.*, unpublished data.