BORON–NITROGEN COMPOUNDS

XXIII* THE VIBRATIONAL SPECTRUM OF 2-METHYL-1,3,2-DIAZABORA-CYCLOHEXANE

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Recently[2], we described a synthesis of 1,3,2-diazaboracyclohexanes (I) which offers ready access to this class of compounds. In continuation of this study of boron–nitrogen–carbon heterocycles, we now report on the vibrational spectrum of a

representative derivative of (I), *i.e.* 2-methyl-1,3,2-diazaboracyclohexane (I, R = CH$_3$, R' = H).

This compound was first prepared by Goubeau and Zappel[3] by pyrolyzing the adduct formed from trimethylborane and 1,3-diaminopropane. The same authors also recorded the Raman spectrum of the compound; however, no detailed assignment of the spectrum was attempted.

Since that time the spectra of a number of acyclic bisaminoboranes[1,4] (II, III) and of 1,8,10,9-triazaboradecalin[5] (IV) have been discussed; data compiled on these compounds can be used for the interpretation of the spectrum of 2-methyl-1,3,2-diaza-boracyclohexane. In addition, the known spectra of *B*-trimethylborazine[6], (–BCH$_3$–NH–)$_3$, and of cyclohexane[7] may be used for assignments of some specific vibrations of this B–N–C heterocycle. However, reasonably certain assignments of many vibrations are possible only by studies with isotopically labeled materials. Therefore,

we have prepared the 2-(trideuteromethyl)-1,3,2-diazaboracyclohexane, as well as the N-dideuterated and the ^{10}B-enriched 2-methyl-1,3,2-diazaboracyclohexane. Data obtained from a study of the spectra of these labeled materials has enabled a more accurate assignment of characteristic vibrational modes.

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* For Part XXII see ref. 1.

A. THE MOLECULAR MODEL

It is known[3] that the free electron pair of nitrogen participates in the bonding between boron and nitrogen through superimposure of π-bonding on a B–N σ-bond (eqn. 1). The planarity or near planarity of the boron–nitrogen covalent bond is a

$$>\text{B}-\ddot{\text{N}}< \quad \longleftrightarrow \quad >\text{B}=\text{N}< \tag{1}$$

prerequisite for such multiple bond formation. Since, due to the sp^2 hybridization, the substituents on the nitrogen will also preferentially be coplanar with the boron bonds, the (V) moiety of the 2-methyl-1,3,2-diazoboracyclohexane molecule should be planar.

$$\text{H}-\overset{|}{\text{N}}\diagdown_{\underset{|}{\text{B}}}\diagup\overset{|}{\text{N}}-\text{H}$$
$$-\overset{|}{\underset{|}{\text{C}}}- \quad (\text{V})$$
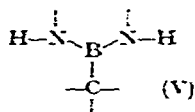
In order to have the simplest possible model as a basis for the discussion it is assumed that all annular atoms are coplanar, and the hydrogen atoms of the methylene groups are symmetrically arranged above and below the ring plane of (I). This assumption provides C_{2v} symmetry and the 18-atomic molecule should exhibit $3 \times 18 - 6 = 48$ vibrations, out of which $7 \times 3 - 6 = 15$ will be skeletal modes.

The model of a completely coplanar ring system as discussed above is actually not quite correct. Examination of a molecular model reveals the out-of-plane distortion of the ring atom 5 of (I) as the most apparent anomaly. However, this distortion should not drastically influence those vibrations of the molecule in which nitrogen or boron participate. Also, the expected vibrations of the C–C–C part of the molecule are deduced from the corresponding vibrations of cyclohexane. Therefore any differences between the discussion model and the actual molecular geometry should be of minor importance with regard to most spectral features and should be largely negligible.

B. THE EXPECTED SPECTRUM

The NH stretching of 2-methyl-1,3,2-diazaboracyclohexane is expected near 3450 cm^{-1}. This conclusion is based on the assumption that the compound will possess a boron–nitrogen bond character similar to that found in B-trimethylborazine, bis-(monoalkylamino)boranes, and 1,8,10,9-triazaboradecalin. If nitrogen is in a planar valence configuration, one would expect NH deformation modes to be in the range of 1300–1400 cm^{-1}; coupling of $\delta(\text{NH})$ with BN stretching vibrations can cause a frequency shift for both modes. However, since N-deuteration results in a frequency decrease of about $1/\sqrt{2}$, this effect should permit unequivocal assignment of NH vibrations. Considering the effect of coupling between BN stretching modes and $\delta(\text{NH})$ vibrations, the antisymmetrical BN$_2$ stretch of 2-methyl-1,3,2-diazaboracyclohexane is anticipated to be in the 1450 cm^{-1} region, whereas $\nu_s(\text{BN}_2)$ should be observed near 1385 cm^{-1}. Definite identification of these BN$_2$ vibrations should be possible through isotope effects, since on the transition of $^{11}\text{B}\rightarrow^{10}\text{B}$, a frequency increase in the order of 10–15 cm^{-1} is likely.

Disregarding the CH stretching modes, which will occur near 2800–3000 cm^{-1}, the grouping CH$_3$–B< should exhibit the following vibrations:

$\delta_{as}(CH_3) \approx 1460$ cm^{-1}

$\delta_s(CH_3) \approx 1300$ cm^{-1}

$\rho(CH_3) \approx 925$ cm^{-1}

$\nu(BC) \approx 880$ cm^{-1}

Deuteration of the methyl group permits discrimination of its absorptions from those of the methylene groups. The hoped for effect of deuteration can be deduced from the analogous data reported for trimethylborane[9] and bis(dimethylamino)methylborane[1]. The observed frequency changes for these two compounds upon deuteration of the B-methyl groups are listed in Table 1.

TABLE 1

FREQUENCY SHIFTS ON DEUTERATION OF THE B-METHYL GROUPS IN TRIMETHYLBORANE AND BIS-(DIMETHYLAMINO)METHYLBORANE

(Frequencies in cm^{-1})

	$\nu_{as}(CH)$	$\nu_s(CH)$	$\delta_{as}(CH_3)$	$\delta_s(CH_3)$	$\rho(CH_3)$	$\nu(BC)^a$
B(CH$_3$)$_3$	~3000	~2900	~1480	1306	970	1156
^{10}B(CH$_3$)$_3$	~3000	~2940	~1460	~1310	985	1178
B(CD$_3$)$_3$	2230	2185	1070	1018	870	1205
CH$_3$B·N(CH$_3$)$_{2\cdot2}$	~3000	~2840	1498	1300	940	878
CH$_3$^{10}B·N(CH$_3$)$_{2\cdot2}$	~3000	~2860	~1460	1302	952	891
CD$_3$B·N(CH$_3$)$_{2\cdot2}$	2210	2180	~1125(?)	1023	790	914

^{a} The value of ν(BC) of the trimethylboranes is that of the antisymmetric stretching vibration. As noted by Lehmann et al.[9] the deuterated compound exhibits a shift of that vibration to a frequency higher than that of the non-deuterated analog; however, this direction of the shift was confirmed by calculations. These observations can be interpreted that on deuteration of the methyl groups the antisymmetric deformation mode assumes the character of ν_{as}(BC) and vice versa (cf. ref. 9).

Since NC stretching vibrations are known to occur in the 1100–1200 cm^{-1} range, only the vibrations of the methylene groups and the CC$_2$ grouping have to be predicted. This can be done on the basis of our previous considerations on the spectrum of 1,8,10,9-triazaboradecalin[5].

C. ASSIGNMENTS

In Table 2 the Raman spectrum (A) and the infrared spectrum (B) of 2-methyl-1,3,2-diazaboracyclohexane are listed along with the infrared spectra of the ^{10}B-enriched compound [(C) 92 % ^{10}B], the N-dideuterated product [(D) ca. 90 % ND] and of 2-trideuteromethyl-1,3,2-diazaboracyclohexane [(E) 96 % CD$_3$]. The infrared spectra were recorded from liquid films in the range 660–2000 cm^{-1} with a Perkin–Elmer Model 21 spectrophotometer; compounds B, D, and E were also recorded in

TABLE 2

VIBRATIONAL SPECTRA OF 2-METHYL-1,3,2-DIAZABORACYCLOHEXANE

(Frequencies in cm⁻¹)ᵃ

A	B	Cᵇ	D	E	Assignments
172 vw					
289 vw					
325 w					
438 m					
484 m					
536 vw					
604 m					
	675 m		674 m		
	730 vw		730 vw		
		741 vw			
769 vs	763 m	764 m	752 m–s	756 m	$\rho(CD_3)$
			762 m	771 vs	$\nu(ring)$
				788 m	$\rho(CD_3)$
	817 m	818 m	813 w–m		
			832 vw		
859 m	853 vw	856 w		851 vw	$\rho(CH_2)$
			872 w–m		$\delta(ND)$
892 vw	887 m–s	890 sh w	887 m–s	888 w	$r(^{11}BCH_3)$
		898 m–s	902 w		$r(^{10}BCH_3)$
				931 m–s	$r(BCD_3)$
	948 m	949 m–s	944 w	943 m	$\gamma(NH) + \rho(CH_3)$
962 m					
			988 s		$\delta(ND)$
992 w					
			1017 w–m		
1030 vw				1036 w–m	$\delta_s(CD_3)$
			1040 m		
			1058 vw		
	1099 w–m	1101 m	1102 sh m	1097 w–m	$\nu(CC_2)$
1110 m	1111 vw	1112 w	1114 s	1111 m	$\nu(NC)$
			1123 sh m		
				1172 sh m	$\delta(NH)$
	1172 vs	1176 sh w		1188 sh s	$r(NC) + \delta(NH)$
1180 s	1186 s	1188 s	1185 m	1197	$\delta_{as}(CD_3)$
	1203 vw	1203 sh m	1202 sh w	1212 sh m	
			1212 s–vs		
			1248 s		
1277 s	1275 sh w	1274 sh w	1272 sh w	1278 sh w	$\tau(CH_2)$
	1293 vs	1294 sh m	1292 sh m	1298 s	
	1310 sh s	1310 vs	1312 vvs	1313 s	$\delta(NH) + \gamma(CH_2) + \delta_s(CH_3)$
1333 m–w	1328 m	1328 sh m	1324 sh w	1329 s–m	$\gamma(CH_2)$
			1356 vvs		
1360 w	1360 vvs	1358 sh m	1365 sh vs	1362 vs	$r_s(^{11}BN_2)$
	1372 sh m	1376 vs	1372 sh m	1374 sh w	$r_s(^{10}BN_2)$
			1401 vvs		
			1423 vvs		
1437 s	1432 s	1434 s	1436 sh vs	1438 sh s	$\delta(CH_2)$
1458 m–w	1448 sh s	1448 sh s	1448 sh vs	1448 vs	$\delta(CH_2)$
	1453 s	1454 s	1458 s		$\delta_{as}(CH_3)$
1480 s	1473 sh s	1480 s	1486 vvs	1478 sh vs	$\delta(CH_2)$
	1492 vvs	1493 sh s	1494 sh vs	1492 vvs	$r_{as}(BN_2)$
	1502 sh vs	1504 vvs	1502 sh m	1501 sh vs	
		1518 sh s			

TABLE 2 (continued)

A	B	C[b]	D	E	Assignments
	1570 w	1578 vw	1572 w		
				2205 m	} ν(CD)
				2214 m	
			2230 w		
			2579 s		ν(ND)
2718 vw				2710 vw	
	2815 sh w			2818 w	
2850 s	2835 sh m		2850 s	2833 m	} ν_s(CH)
	2847 s			2847 s	
	2858 s			2859 s	
	2908 s		2908 s	2910 s	
2905 vs	2930 vs		2927 vs	2930 vs	} ν_{as}(CH)
	2950 s		2949 vs	2948 s	
			2968 sh m		
3465 s	3474 s		3468 w–m	3474 s	ν(NH)

[a] w = weak; m = medium; s = strong; v = very; sh = shoulder. [b] Not measured above 2000 cm^{-1}.

CCl$_4$ solution in the range 2000–4000 cm^{-1} with a Perkin Elmer Model 421 instrument. The Raman spectrum was taken of the pure liquid using a Cary Raman spectrometer Model 81.

For a reasonably and essentially complete assignment of the spectra on the basis of the above discussion, intensities and band shapes of the infrared spectra were also considered. Nevertheless, eventual revision of certain assignments, especially those concerning vibrations of the (CH$_2$)$_3$ part of the molecule cannot be excluded.

D. THE BONDING IN 2-METHYL-1,3,2-DIAZABORACYCLOHEXANE

The relatively high frequency of the NH stretching vibration is somewhat surprising; its value of 3474 cm^{-1} is considerably higher than that found for B-trimethylborazine (ν(NH) = 3408 cm^{-1}). The high frequency of ν_{as}(BN$_2$) (even recognizing the effect of coupling of δ(NH) and ν(BN$_2$), which results in a frequency increase of the latter) can be construed as evidence for a high B–N bond order in 2-methyl-1,3,2-diazaboracyclohexane, and, simultaneously, it supports the planarity of the CBN$_2$ part of the molecule.

The extremely strong Raman band at 769 cm^{-1} has already been accepted by Goubeau and Zappel[2] as ring pulsation. This vibration is identical in frequency as well as in intensity to the strongest skeletal vibration of methylcyclohexane and similar monosubstituted ring systems. This observation then substantiates the cyclic structure of the compound in question. Almost certainly no ring strain is present in the system. Since one has to assume a large force constant, k_{BN}, the boron–nitrogen–carbon heterocycle should be thermally quite stable. This postulation is confirmed by experiment.

E. EXPERIMENTAL

2-Methyl-1,3,2-diazaboracyclohexane was obtained by the transamination of bis(dimethylamino)methylborane with 1,3-diaminopropane as described previously[2].

For the preparation of the N-dideuterated material, 1,3-diaminopropane was treated several times with D_2O (acidified with a drop of D_2SO_4) and subsequently was distilled over BaO. The partially N-deuterated amine was transaminated with bis(dimethylamino)methylborane, the resultant BNC-heterocycle was deuterolized and the deuterated 1,3-diaminopropane was isolated, dried and again was subjected to a transamination reaction. The resultant deuterated 2-methyl-1,3,2-diazaboracyclohexane was estimated (by NMR) to contain approx. 90% ND.

For the preparation of the [10]B-enriched derivatives, commercially available boric acid with a content of 92% [10]B was transformed into boron trichloride[10]. Part of the BCl_3 was aminolized to tris(dimethylamino)borane[11], which then was rearranged with the remaining BCl_3 to yield bis(dimethylamino)chloroborane[12]. Reaction of the latter with Grignard reagent provided for bis(dimethylamino)methylborane[13], which subsequently was transaminated with 1,3-diaminopropane. The B-trideuteromethyl derivative was prepared in an analogous fashion, utilizing the commercially available trideuteromethyl iodide in the Grignard process.

All operations were performed in an argon atmosphere to minimize contamination of the agents. Purity was controlled by ^{1}H nuclear magnetic resonance spectroscopy and, in most cases, also by vapor phase chromatography.

SUMMARY

Major absorptions of the vibrational spectrum of 2-methyl-1,3,2-diazaboracyclohexane have been assigned by utilizing isotopically labeled materials. The spectroscopic data confirm the previously proposed structure of the compound. The nature of the chemical bonding in this boron–nitrogen–carbon heterocycle is discussed briefly.

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