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Boron-Nitrogen Compounds. XXVI.[1,2] A Spectroscopic Study of Dimethylaminovinylbromoborane

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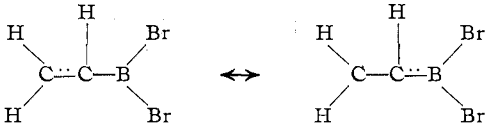
The infrared spectrum of dimethylaminovinylbromoborane, $(CH_3)_2NBBrCH{=}CH_2$, in the 300–4000-cm^{-1} range has been recorded and fundamental vibrations have been identified utilizing data derived from the Raman and infrared spectra of bis(dimethylamino)vinylborane, $CH_2{=}CHB[N(CH_3)_2]_2$. Also, the proton magnetic resonance spectrum of dimethylaminovinylbromoborane has been studied and, on the basis of chemical shift data obtained at various temperatures, a barrier to rotation about the B–N axis of the molecule of the order of magnitude of 14.0 ± 0.4 kcal/mole has been calculated. Evaluation of the spectroscopic data permits a discussion of the bonding in the molecule.

Introduction

The existence of B–C π bonding in vinyl derivatives of boron was originally postulated by Ritter and coworkers[4,5] and later was substantiated by some physicochemical studies.[6,7] More recently,[8] a detailed investigation of the vibrational spectrum of vinyldibromoborane, $CH_2{=}CHBBr_2$, established that the valence force constant k(BC) in this compound is substantially increased when compared with that of trimethylborane, $B(CH_3)_3$, or methyldibromoborane, CH_3BBr_2. Also, the force constant k(CC) of vinyldibromoborane is clearly smaller than the corresponding constant of ethylene or of the double bond in propylene. Therefore, it is reasonable to consider the existence of electron delocalization in the vinyldibromoborane molecule as indicated in



(1)

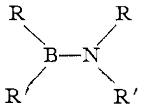
This postulation is in agreement with the results of an LCAO moleculear orbital treatment[7] which resulted in a B–C bond order of 1.35 for the B–C$_{vinyl}$ linkage in dimethylvinylborane, $(CH_3)_2BCH{=}CH_2$.

On the other hand, it is known that the free electron pair of a nitrogen attached to a boron atom can participate in the B–N bonding thereby effecting a certain degree of double-bond character

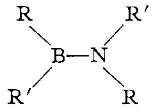
(2)

The B–N stretching frequency of boron–nitrogen compounds has often been related to the bond order. Since the vibrational frequencies are influenced by coupling with other modes, the νBN will not give an accurate picture of the bonding. It can be used only for a rough evaluation of bond order data whereas the valence force constants can be related more directly to the bond order than vibrational frequencies. However, in most cases, the calculation of the force constants involves a considerable mathematical treatment which normally limits the application of this method to a study of simple molecules containing only a relatively small number of atoms.

A more convenient method designed to evaluate the bond order of aminoboranes, $R_2NBR'_2$, has been developed in recent years. As noted above, participation of the free electron pair of the nitrogen in the B–N linkage provides a certain degree of B–N double-bond character (eq 2). If the B–N π bonding is strong enough, one can expect an appreciable barrier to rotation about the B–N axis of the molecule, and *cis* and *trans* isomers may be expected in the case of unsymmetrically substituted aminoboranes (I, II). The

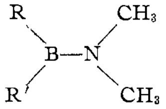


I
(*cis*)



II
(*trans*)

existence of aminoborane rotational isomers was originally suggested by Niedenzu and Dawson[9] and was subsequently confirmed by nmr studies.[10,11] The barrier to rotation provides information about the degree of π bonding and hence the bond order. Such data can be obtained by a simple procedure. For example, the two methyl groups of a compound of type III will



III

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[1] Part XXV: W. Weber, J. W. Dawson, and K. Niedenzu, *Inorg. Chem.*, **5**, 726 (1966).

[2] Supported by the U. S. Army Research Office, Durham, N. C.

[3] Visiting Lecturer from the Laboratorium für anorganische Chemie, Technische Hochschule, Stuttgart, Germany.

[4] T. D. Parsons and D. M. Ritter, *J. Am. Chem. Soc.*, **76**, 1710 (1954).

[5] T. D. Parsons, M. B. Silverman, and D. M. Ritter, *ibid.*, **79**, 5091 (1957).

[6] T. D. Coyle, S. L. Stafford, and F. G. A. Stone, *J. Chem. Soc.*, 3103 (1961).

[7] C. D. Good and D. M. Ritter, *J. Am. Chem. Soc.*, **84**, 1162 (1962).

[8] K. Niedenzu and W. Sawodny, *Z. Anorg. Allgem. Chem.*, **344**, 179 (1966).

[9] K. Niedenzu and J. W. Dawson, *J. Am. Chem. Soc.*, **82**, 4223 (1960).

[10] G. E. Ryschkewitsch, W. S. Brey, Jr., and A. Saji, *ibid.*, **83**, 1010 (1961).

[11] P. A. Barfield, M. F. Lappert, and J. Lee, *Proc. Chem. Soc.*, 421 (1961).

TABLE I

VIBRATIONAL SPECTRUM OF BIS(DIMETHYLAMINO)VINYLBORANE

Raman	Infrared	Assignment
247 w, dp		Skeletal def
	340 vw	
365 mw, dp		
	395 w	
479 vw, b		
557 w		
	608 vw	
620 m, p		τCH_2
	682 m	
691 w, dp		
	699 sh	
	800 m	
	878 mw	
890 sh	891 m	νBC
903 w, dp	902 sh	
	941 s	$\gamma CH'$
954 mw, dp		
1026 w, p?	1013 s	γCH_2
1070 w, dp	1058 s	$\nu_s NC$
1101 mw, p	1102 m	$\nu_{as}NC + \rho CH_3$
	1125 s	
1142 w, b, dp	1142 m	
	1192 ms	
	1212 s	ρCH_3
	1236 s	ρCH_3
1289 m, p	1302 m	$\delta CH'$
	1350 mw	
1363 m, p		
	1382 vs	$\nu_s BN_2$
	1392 sh	
	1404 w	
1420 s, p	1422 w	δCH_2
1447 s, dp	1444 vs	δCH_3
	1456 m	
1488 sh	1495 vs	
1512 vs	1506	$\nu_{as}BN_2$
	1520 sh	
1609 vs, p	1603 s	νCC
	1746 vw	
	1888 vw	
	1990 vw	
	2080 vw	
	2120 vw	
	2400 vw	
2507 w	2500 vw	
2798 s, p	2785 sh	νCH
2852 sh, p	2860 vs, b	
2874 vs, dp		
2924 s, p	2920	
2972 vs, p	2965	
2988 sh, dp		
3054 s, dp	3048 m	

[a] Frequencies in cm^{-1}: w, weak; m, medium; s, strong; v, very; b, broad; sh, shoulder; p, polarized; dp, depolarized.

be in different chemical environments if there is hindered rotation about the B–N linkage. This event is then evidenced by the appearance of two distinct ^1H resonances for the CH_3 groups when the pmr spectrum of the compound is recorded. Rotation about the B–N axis increases with temperature and at a certain point one no longer can distinguish two separate peaks for the two methyl resonances, indicating virtually free rotation. From such data the barrier to rotation due to the B–N double-bond character as depicted in eq 2 has been calculated for a variety of aminoboranes;[12] potential barriers on the order of 14–20 kcal/mole have been reported.

A point of interest exists as to whether or not a competition obtains for the vacant p_z orbital of a boron atom between the π electrons of a boron-bonded vinyl group and the free electron pair of an amino group bonded to the same boron atom. Therefore, we have investigated the vibrational spectrum of dimethylaminovinylbromoborane, $(CH_3)_2NBBrCH{=}CH_2$, in the 300–4000-cm^{-1} range. Owing to the high fluorescence of the compound, no useful Raman spectrum could be obtained. Since this lack of information may result in erroneous assignments of major vibrational modes, Raman and infrared spectra of bis(dimethylamino)vinylborane, $CH_2CHB[N(CH_3)_2]_2$, were recorded and interpreted as supporting evidence. Based on these data, the proposed assignments of fundamental vibrations of dimethylaminovinylbromoborane appear to be reasonably certain and a rough evaluation of the bonding within the molecule can be realized. A more refined picture of the bonding situation is obtained through additional studies of the compound by nuclear magnetic resonance spectroscopy, particularly by investigating the influence of varying temperature on the behavior of proton resonance lines.

Experimental Section

Bis(dimethylamino)vinylborane and dimethylaminovinylbromoborane were prepared by previously reported procedures.[13] Infrared spectra of films of the neat liquid compounds were recorded with a Perkin-Elmer Model 621 spectrophotometer in the 300–4000-cm^{-1} region. Raman spectra were obtained with a Cary Raman spectrometer, Model 81. Proton magnetic resonance spectra were recorded of the neat liquids with a Varian A-60 high-resolution nmr spectrometer using tetramethylsilane sealed in capillary tubes as an internal standard. For the studies of the temperature dependence of nmr lines, a Varian V-6040 variable-temperature accessory was employed. Calculations were carried out with an IBM Model 7020 computer utilizing an iterative method.

The Vibrational Spectrum of Bis(dimethylamino)vinylborane

The vibrational spectrum of bis(dimethylamino)vinylborane shows the expected complexity of such a polyatomic molecule and cannot be interpreted completely. Table I lists the spectrum of the compound including the assignments made for the various vibrational modes. No uncertainties exist in the region above 1600 cm^{-1}.

According to Becher,[14] symmetrical CH_3 deformational modes of dimethylaminoboranes couple strongly

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[12] H. Watanabe, T. Totani, K. Tori, and T. Nakagawa, Proceedings, XIIth Colloque Ampére, Leuven, 1964, p 374, and references cited therein.

[13] P. Fritz, K. Niedenzu, and J. W. Dawson, *Inorg. Chem.*, **3**, 626 (1964).

[14] H. J. Becher, personal communication; H. J. Becher and H. T. Baechle, *Z. Physik. Chem.* (Frankfurt), **48**, 360 (1966).

with B–N stretching vibrations, and assignments in the 1450–1500-cm^{-1} region cannot be made unequivocally. However, comparing the present data with the spectrum of bis(dimethylamino)methylborane,[15] the antisymmetric BN_2 stretching mode of bis(dimethylamino)vinylborane can be assigned at 1506 cm^{-1} and $\nu_s BN_2$ at 1382 cm^{-1}. It is difficult to discriminate between ρCH_3 vibrations and $\nu_{as}NC_2$ in the 1100–1200-cm^{-1} region; $\nu_s NC_2$ can probably be assigned at 1064 cm^{-1} and the B–C stretching mode is identified at 891 cm^{-1}. Most of the remaining assignments are based on a comparison of the present data with the spectra reported for bis(dimethylamino)methylborane[15] and vinyldibromoborane.[8]

No reasonable interpretation can be made for the absorption at 1357 cm^{-1}. This band which is normally of medium to strong intensity has been consistently observed in the 1355–1365-cm^{-1} region of the infrared spectra of a variety of B-vinylated boranes.

The Infrared Spectrum of Dimethylaminovinylbromoborane

On the basis of the preceding discussion of the vibrational spectrum of bis(dimethylamino)vinylborane, several assignments of vibrational modes observed in the infrared spectrum of dimethylaminovinylbromoborane can be made with reasonable certainty. The spectrum of the latter compound is listed in Table II.

TABLE II

INFRARED SPECTRUM OF DIMETHYLAMINOVINYLBROMOBORANE[a]

Freq, cm^{-1}	Assignments	Freq, cm^{-1}	Assignments
338 m		1367 vw	
518 m		1402 sh	δCH_2
655 s	νBBr	1422 vs	νBN
665 sh		1449 m	δCH_3
678 sh		1461 m	
698 vw		1484 mw	
748 w		1505 sh	δCH_3
780 m		1512 vs	
813 mw		1530 sh	
868 s		1548 sh	
938 sh	$\gamma CH'$	1604 s	νCC
959 s	νBC	1923 w	
1000 m		2352 vw	
1026 vw	γCH_2	2795 ms	νCH
1060 sh	$\nu_s NC + \rho CH_3$	2868 w	
1074 s		2928 vs	
1140 s	$\nu_{as}NC + \rho CH_3, \rho CH_2$	2984 w	
1197 s		3012 wm	
1295 vw	$\delta CH'$	3064 mw	

[a] Frequencies in cm^{-1}: w, weak; m, medium; s, strong; v, very; sh, shoulder.

The B–N stretching vibration is identified at 1422 cm^{-1}, and νBC is tentatively assigned at 959 cm^{-1}. These observations appear to be of some significance. In the spectrum of vinyldibromoborane, νBC was assigned at 991 cm^{-1}. Replacing the bromine atoms of $CH_2{=}CH{-}BBr_2$ successively by dimethylamino groups results in a lowering of the BC frequency to 959 and 891 cm^{-1}, respectively. If this frequency decrease is not due to a coupling effect, this observation would indicate a corresponding decrease in the force constant $k(BC)$. In other words, the lone pair of electrons of the amino group participates in the B–N bonding, thus reducing the electron deficiency at the boron atom and thereby lessening the degree of B–C π bonding. This circumstance, however, is not apparent from the frequency of the C=C stretching mode, which is consistently observed in the spectra of B-vinylated boranes at 1605 ± 10 cm^{-1}, independently of the nature of the other substituents.

The Proton Magnetic Resonance Spectrum of Dimethylaminovinylbromoborane

The ^1H nmr spectrum of dimethylaminovinylbromoborane at room temperature shows two distinct sets of resonance lines. A broad and unresolved multiplet structure centered near τ 3.52 ppm has been assigned to the resonance of the protons of the vinyl group. On the other hand, the two methyl groups of the molecule exhibit two sharp and distinct lines of equal intensity near τ 6.70 and 6.78 ppm, respectively. This observation indicates the presence of two sets of ^1H nuclei for the methyl groups of dimethylaminovinylbromoborane, which are in two chemically different but equally abundant environments.

As the sample is heated, the two methyl proton resonance bands broaden and the separation between the peaks decreases until they finally coalesce at a temperature T_c near 125°. This event appears attributable to hindered rotation about the B–N linkage of the molecule due to B–N π bonding. On the basis of the temperature-dependent spectral changes, the barrier to rotation about the B–N axis of the molecule has been calculated using the analytical methods for the evaluation of such data as developed by Gutowsky and Holm.[16]

The results of several recordings of the changes of peak separation $\delta\omega_e$ of the two methyl resonances of dimethylaminovinylbromoborane with varying temperature T are summarized in Table III. In the absence of exchange effects or overlap of components, the width of each methyl resonance band at half-maximum peak height is $2/T_2$ where T_2 is the transverse relaxation time; $2/T_2$ was found to be essentially constant in the temperature range from −10 to +40° with a value of 1.31 ± 0.01 cps. Over the same temperature range, the maximum separation of the two methyl resonance lines, $\delta\omega_\infty$, was found to be constant with a value of 5.10 ± 0.05 cps. The activation energy, E_a, was obtained from a plot of log $(1/t\delta\omega_e)$ *vs.* $1/T$, where t is half of the methyl proton site lifetime by a least-square fit. It is quite insensitive to changes in $2/T_2$ and was calculated to be 14.0 ± 0.4 kcal/mole. The frequency factor ν^0, the internal torsional frequency, was found to be in the order of 10^9 sec^{-1}.

Discussion

It has been established[17] that a boron-bonded vinyl group tends to afford a certain degree of B–C π bonding

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[15] J. W. Dawson, P. Fritz, and K. Niedenzu, *J. Organometal. Chem.* (Amsterdam), **5**, 13 (1966).

[16] H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).

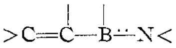
[17] See ref 8 and literature cited therein.

Table III

Barriers to Rotation about the B–N Bond of Dimethylaminovinylbromoborane

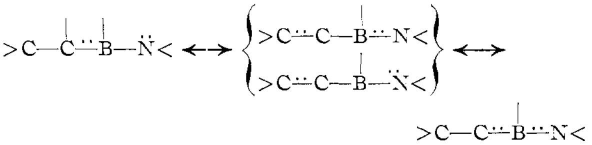
T, °C	$\delta\omega_e$, cps			
	I	II	III	IV
50	5.10	5.10	5.10	5.10
90	4.90	4.95	4.95	4.95
110	4.00	4.40	4.60	4.10
115	3.46	4.20	3.85	3.60
120	2.20	3.35	3.10	2.80
125	Merged	1.50	1.30	Merged
127		Merged	Merged	
E_a, kcal/mole	14.40 ± 0.2	13.63 ± 0.2	13.74 ± 0.3	14.27 ± 0.2

by delocalization of the π electrons of the carbon–carbon double bond (*cf.* eq 1). The free electron pair of the nitrogen atom of an aminoborane can also participate in the bonding[18] (*cf.* eq 2). Therefore, the π electrons of these two substituent groups on the boron of an aminovinylborane will compete for the vacant p_z orbital of the boron atom. On this basis, the existence of a dienic configuration (IV) is unlikely


$>\mathrm{C{=}\overset{|}{C}{-}\overset{|}{B}}\cdots\mathrm{N}<$

IV

to predominate in the electronic equilibrium of an aminovinylborane. Rather, one must anticipate a situation as depicted in eq 3. Which of the possible


$$>\mathrm{C{-}\overset{|}{C}}\cdots\overset{|}{\mathrm{B}}{-}\ddot{\mathrm{N}}< \longleftrightarrow \left\{\begin{matrix} >\mathrm{C}\cdots\mathrm{C}{-}\overset{|}{\mathrm{B}}\cdots\mathrm{N}< \\ >\mathrm{C}\cdots\mathrm{C}{-}\overset{|}{\mathrm{B}}{-}\ddot{\mathrm{N}}< \end{matrix}\right\} \longleftrightarrow >\mathrm{C{-}C}\cdots\overset{|}{\mathrm{B}}\cdots\mathrm{N}<$$

(3)

alternates is predominant will depend on the π-electron donor strength of the two groups bonded to the boron atom.

An evaluation of the vibrational spectra of the bis(dimethylamino)vinylborane (A) and dimethylaminovinylbromoborane (B) appears to indicate a relatively high B–N bond order for aminovinylboranes. The B–N stretching frequency is found near 1430 cm^{-1} (A: $\nu_{as}BN_2$ 1506 cm^{-1}, $\nu_s BN_2$ 1382 cm^{-1}, mean value 1444 cm^{-1}; B: νBN 1420 cm^{-1}). However, present facilities do not permit the calculation of the valence force constants, which should provide a better correlation with the bond order than the vibrational frequencies.

The C=C stretching frequency of A and B is observed near 1604 cm^{-1}. This relatively low value may indicate a slight decrease in the double bonding between the carbon atoms of the vinyl group as compared to ethylene. This interpretation of the data finds support from some ultraviolet studies. The ultraviolet spectrum of bis(dimethylamino)vinylborane is similar to that of dimethylvinylborane[7] and exhibits a main band at 218 mμ. Table IV lists ultraviolet absorption bands of some vinylated boranes. It is quite apparent that the band associated with the vinyl group undergoes a clear bathochromic shift as compared to that of ethylene (162 mμ).

Table IV

Ultraviolet Absorptions of Some Vinylboranes

Compound	λ_{max}, mμ	Ref
$(CH_3)_2BCH{=}CH_2$	196	7
$[(CH_3)_2N]_2BCH{=}CH_2$	218	This work
$(CH_3)ClBCH{=}CH_2$	206	7
$[(CH_3)_2N]BrBCH{=}CH_2$	223	This work

On the other hand, a potential barrier to rotation about the B–N bond of dimethylaminovinylbromoborane of 14.0 ± 0.4 kcal/mole has been calculated based on nmr experiments. Utilizing the procedure as previously outlined by Watanabe, *et al.*,[12] a relative π-bond order of about 0.45 is calculated for the B–N bond of the compound. This value compares favorably with that of dimethylaminophenylchloroborane.[12] In other words, the effect of a boron-bonded vinyl group on the B–N bond order of an aminovinylborane appears to be of the same character and the same order of magnitude as in a comparable aminophenylborane. For the latter type of compound a certain degree of B–C_{aryl} π bonding corresponding with a decrease in the B–N bond order had been deduced from experimental data[19] and was confirmed by an independant molecular orbital treatment.[20] On the basis of the present data, it is therefore evident that an increase in the B–N bond order of an aminovinylborane through a conjugation effect as depicted in IV is not likely, and structure IV appears not to contribute to the electronic equilibrium of the molecule.

In dimethylaminovinylbromoborane, the nitrogen is a stronger π-electron donor than the vinyl group, as is indicated by the degree of B–N double-bond character. Nevertheless, the B–N bond order of the aminovinylborane is somewhat diminished when compared to a corresponding aminoalkylborane. As a matter of fact, on the basis of an analogous evaluation,[12] the B–N double-bond character ρBN of dimethylaminovinylbromoborane is even somewhat smaller than that of dimethylaminophenylchloroborane (see Table V). This observation implies that a boron-bonded vinyl group is a stronger electron donor than is the phenyl group. This conclusion cannot be reached from a consideration of the vibrational spectra.

Table V

B–N Double-Bond Character of Some Aminoboranes

Compound	E_a, kcal/mole	νBN, cm^{-1}	ρBN
Dimethylaminophenylethylborane	19.7	1413	0.63
Dimethylaminophenylchloroborane	15.2	1415	0.49
Dimethylaminovinylbromoborane	14.0	1420	0.45

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[18] K. Niedenzu and J. W. Dawson, "Boron-Nitrogen Compounds," Springer-Verlag, Berlin, 1965.

[19] G. M. Wyman, K. Niedenzu, and J. W. Dawson, *J. Chem. Soc.*, 4068 (1962).

[20] J. J. Kaufman and J. R. Hamann, Advances in Chemistry Series, No. 42, American Chemical Society, Washington, D. C., 1964, p 95.