1008. *Infrared Spectra of Open-chain Boron–Nitrogen Compounds.*

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The infrared spectra of 20 boron compounds of types $B(NR_2)_3$, $B(NRAr)_3$, $B(NHR)_3$, $B(NHAr)_3$, $(R''O)_nB(NRR')_{3-n}$ ($n = 1$ or 2), and R″O·BCl·NRR′ have been recorded and complete assignments have been proposed for four representative compounds. The ^{11}BN asymmetric stretching frequency lies at 1353 [$B(NMePh)_3$], 1430 ± 20 [$B(NR_2)_3$], 1495 [$B(NHR)_3$], and 1510 cm.$^{-1}$ [$B(NHPh)_3$], while the CN (asymmetric) stretching frequency is found at ~1150 (aliphatic) and ~1300 cm.$^{-1}$ (aromatic). The NH stretching vibration in appropriate compounds is at higher frequencies and is of greater intensity than in amines. The BO (asymmetric) stretching vibrations in compounds $(Bu^nO)_2B{\cdot}NRR'$ lie at lower frequencies than in trialkyl borates. The results are discussed, and four independent lines of evidence show that there is considerable double-bond character in the B·N bonds. The B–N bond strengths decrease in the series $B(NHPh)_3 > B(NHR)_3 > B(NR_2)_3 > B(NMePh)_3$ and the ability to form π-bonds to boron decreases in the series N > O > Cl.

THE infrared spectra of a number of borazans, XYZB·NRR′R″ (*e.g.*, $Me_3B{\cdot}NH_3$; *i.e.*, compounds in which boron has co-ordination number 4),[1-3] and borazens, XYB·NRR′ (*e.g.*, $Me_2B{\cdot}NHMe$; *i.e.*, compounds in which boron has co-ordination number 3),[2-7] have been published. In general, studies have been restricted to the lowest homologues, but complete assignments have been made on some of these compounds, *e.g.*, by assuming D_3 symmetry for $B(NMe_2)_3$.[6] It is generally agreed that in the borazens there is some double-bond character in the B·N bond, due to p_π–p_π-overlap, whilst in the borazans, where this is not possible, the characteristic absorption due to the B·N stretching vibration lies at much lower frequency. However, assignments for the ^{11}BN stretching frequency in borazens vary from 1193·5 (in $H_2B{\cdot}NMe_2$) [2] to 1530 cm.$^{-1}$ (in $Me_2B{\cdot}NMe_2$).[3] Accordingly, we have examined the spectra of a larger number of compounds, all of which are in related homologous series: $B(NR_2)_3$, $B(NHR)_3$, $(R''O)_nB(NRR')_{3-n}$ ($n = 1$ or 2), and R″O·BCl·NRR′.

Trisdialkylaminoborons, $B(NR_2)_3$.—The compounds investigated were those where R = Me, Et, or Bu^n, or R_2N = piperidino. By analogy with the trialkyl borates, in which the BO asymmetric stretching frequency lies at ~1350 cm.$^{-1}$ (and is by far the most intense band),[8] the corresponding BN mode in the aminoborons would be expected to lie in the region 1200—1500 cm.$^{-1}$. All the compounds absorb strongly in this range, but, with the exception of the spectrum of trisdi-n-butylaminoboron (see Fig. and Table 1), in which a band of outstanding intensity lies at 1414 cm.$^{-1}$, there is no one band which predominates in intensity, and unequivocal assignments are therefore not easily made. However, again by analogy with the trialkyl borates, in which the BO asymmetric stretching frequency appears to be almost insensitive to the nature of the alkyl group, the same feature would be expected for the BN frequency in related series of borazens. The assignments which we therefore propose for the ^{11}BN asymmetric stretching frequencies for the remaining aliphatic compounds are 1449 (Me), 1414 (Et), and 1419 (C_5H_{10}) cm.$^{-1}$.

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[1] Goubeau and Becher, *Z. anorg. Chem.*, 1952, **268**, 1, 133; Rice, Galliano, and Lehmann, *J. Phys. Chem.*, 1957, **61**, 1222; Goubeau and Mitschelen, *Z. phys. Chem.*, 1958, **14**, 61; Luther, Mootz, and Radwitz, *J. prakt. Chem.*, 1957, **5**, 242; Taylor and Cluff, *Nature*, 1958, **182**, 390; Katritzky, *J.*, 1959, 2049; Greenwood and Wade, *J.*, 1960, 1130; Kynaston, Larcombe, and Taylor, *J.*, 1960, 1772.

[2] Price, Fraser, Robinson, and Longuet-Higgins, *Discuss. Faraday Soc.*, 1950, **9**, 131.

[3] Becher, *Z. anorg. Chem.*, 1953, **271**, 243.

[4] Bellamy, Gerrard, Lappert, and Williams, *J.*, 1958, 2412.

[5] Becher and Goubeau, *Z. anorg. Chem.*, 1952, **268**, 113; Goubeau, Rahtz, and Becher, *ibid.*, 1954, **275**, 161.

[6] Becher, *Z. anorg. Chem.*, 1956, **287**, 285.

[7] Becher, *Z. anorg. Chem.*, 1957, **289**, 262.

[8] Werner and O'Brien, *Austral. J. Chem.*, 1955, **8**, 355.

The value for trisdimethylaminoboron is made more definite by the presence of a weaker band at 1471 cm.$^{-1}$, which can be assigned to the ^{10}BN asymmetric stretching vibration. The separation of these presumed ^{11}BN and ^{10}BN bands, and their relative intensities, would be consistent with the interpretation. On the other hand, it should be noted that Becher [6] attributed the band at 1384 cm.$^{-1}$ to ^{11}BN and the weaker one at 1413 cm.$^{-1}$ to ^{10}BN. We prefer our assignment, because then the 1509, 1413, and 1384 cm.$^{-1}$ bands remain for CH_3 deformations; in support, we note that *NN*-dimethylformamide [9] (where the NMe_2 group is also attached to an electronegative substituent) has bands of comparable intensities at 1502, 1410, and 1391 cm.$^{-1}$, which in that compound can only arise from CH_3 deformations.

TABLE 1. *Frequencies and assignments of absorption bands in representative borazens.*

Frequency (cm.$^{-1}$) [a]		
$B(NHMe)_3$	$B(NBu^n{}_2)_3$ [g]	Assignment [b]
3420 (1)		N–H stretch
2911 (2)	2928 (1)	C–H stretch
2865 (3)	2890 (2)	
2770 (4)		
1499 (5)		B–N as. stretch
	1486 (3)	C–H deform
	1466 (4)	CH_2 deform
	1414 (5)	B–N as. stretch
1435 (6)		CH_3 deform
1386 (7)	1379 (6)	
	1357 (7)	?
1277 (8)	1290 (8)	CH_3 wagging
	1250 (9)	CC skeletal
	1236 (10)	
	1212 (11)	NC_2 as. stretch
1189 (9)		CH_3 wagging
1139 (10)		C–N stretch
1027 (11)		CH_3 wagging
714 (12)		N–H deform
704 (13)		
$B(NHPh)_3$	$B(NMePh)_3$	
3390 (1)		N–H stretch
3040 (2)	3030 (1)	C–H stretch (A_1)
2899 (3)	2900 (2)	C–H stretch [c]
2849 (4)	2841 (3)	
1942 (5)	1944 (4)	Arom. overtone and combination bands
1862 (6)	1850 (5)	
1792 (7)	1787 (6)	
1730 (8)	1715 (7)	

Frequency (cm.$^{-1}$) [a]		
$B(NHPh)_3$	$B(NMePh)_3$	Assignment [b]
1600 (9)	1595 (8)	C–C stretch (A_1)
1587 [d] (10)	1571 (9)	C–C stretch (B_1)
1510 (11)		B–N as. stretch [e]
	1493 (10)	C–C stretch (A_1)
1471 (12)	1475 [f] (11)	C–H deform [c]
1437 (13)	1431 (12)	C–C stretch (B_1)
1379 (14)		CH_3 deform [c]
	1367 (13)	^{10}B–N as. stretch
	1353 (14)	^{11}B–N as. stretch
1334 (15)	1330 (15)	C–C stretch (B_1)
1314 (16)		?
1300 (17)	1300 (16)	C–H deform (B_1)
1266 (18)	1285 (17)	C_{ar}–N stretch
1218 (19)	1203 (18)	? (mass-dependent, A_1?)
1178 (20)	1189 (19)	C–H deform (A_1)
1154 (21)	1156 (20)	C–H deform (B_1)
	1122 (21)	?
	1106 (22)	C_{al}–N stretch
1079 (24)	1087 (23)	C–H deform (B_1)
	1044 (24)	? (CH_3 wagging?)
1028 (25)	1031 (25)	C–H deform (A_1)
998 (26)	994 (26)	Ring deform (A_1)
900 (27)	896 (27)	C–H deform (B_2)
836 (28)	832 (28)	C–H deform (A_2)
	789 (29)	?
760 (29)		N–H deform?
749 (30)		
740 (31)	762 (30)	C–H deform (B_2)
697 (32)	696 (31)	Ring deform (B_2)

[a] Number in parentheses after each quoted frequency refers to location in appropriate Fig. 1—4. [b] Aromatic vibrations are designated A_1, A_2, B_1, or B_2, as appropriate (cf. Whiffen, *J.*, 1956, 1350). [c] Absorption due wholly, or in part, to liquid paraffin. [d] This band also has contribution from N–H deformation. [e] This band also has contribution from C–C stretch (A_1). [f] The intensity of this band makes it possible that there is an additional contribution from an unassigned mode. [g] Bands lower than 1200 cm.$^{-1}$ are not included.

Assignments of CN stretching frequencies are discussed below (p. 5242).

The spectrum of tri(methylphenylamino)boron, $B(NMePh)_3$, is reproduced in Fig. 2 and assignments are shown in Table 1. The most intense band is at 1353 cm.$^{-1}$, which suggests that this arises from the ^{11}BN asymmetric stretching vibration, and moreover there are indications of $^{11}B/^{10}B$ isotopic splitting. Also noteworthy is the doublet at 1595 and 1571 cm.$^{-1}$ (aromatic CC).

Trisalkylaminoborons, $B(NR)_3$.—These compounds have spectra which are very similar to one another and are each characterised by the presence of three very strong bands in regions 1500 ± 10, 1260 ± 10, and ~1150 cm.$^{-1}$, of progressively decreasing intensities; the appearance of these features is therefore of diagnostic value for the class of compound.

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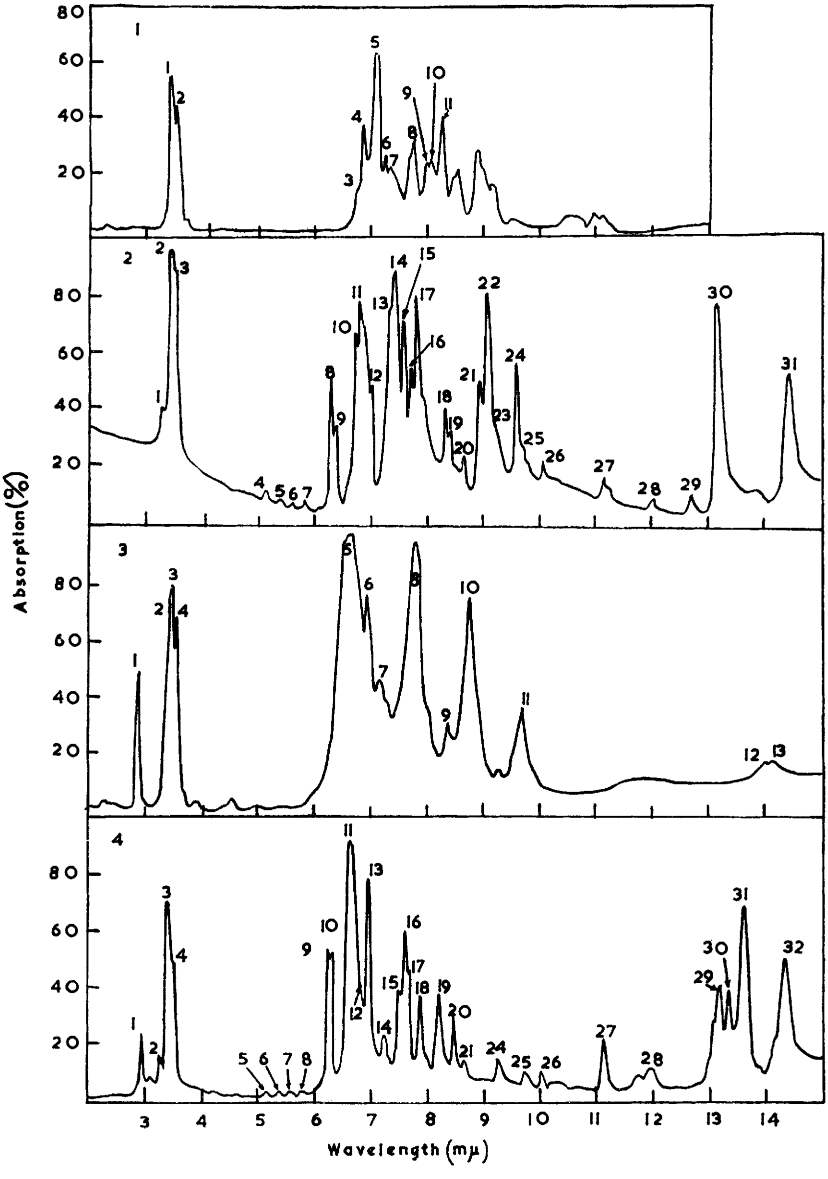
[9] Gerrard, Lappert, Pyszora, and Wallis, *J.*, 1960, 2144.

The band of highest intensity undoubtedly arises from the ^{11}BN asymmetric stretching mode, and the one at lowest frequency is taken as the corresponding CN mode (see p. 5242). The spectrum of trismethylaminoboron, B(NHMe)$_3$, is reproduced in Fig. 3 and assignments are detailed in Table 1.

FIG. 1. *Trisdi-n-butylaminoboron*; 2, *tri(methylphenylamino)boron*; 3, *trismethylaminoboron*; 4, *trisphenylaminoboron.*



It is significant that the NH stretching frequencies in the trisalkylaminoborons are of fair intensity, unlike those in the amines, and that there is a shift to higher frequencies compared with the amines. The spectra of the carbon tetrachloride solutions of the ethyl and the cyclohexyl derivative were also examined; in each case the position and intensity of the NH stretching frequency were independent of concentration.

In trisphenylaminoboron, $B(NHPh)_3$, the aromatic absorption in the 1600 cm.$^{-1}$ region again appeared as a doublet (1595 and 1570 cm.$^{-1}$); the spectrum is reproduced in Fig. 4 and assignments are listed in Table 1.

Further details are summarised in Table 2.

Other Borazens.—The compounds examined were certain oxygen compounds (Table 3) and bisdiethylaminoboron chloride, $Cl{\cdot}B(NEt_2)_2$. In general, the spectra were characterised by having many strong absorption bands in the 1530—1170 cm.$^{-1}$ region, but the band of outstanding intensity (Table 3) (except in bisdiethylaminoboron chloride) is likely to be that due to the BO stretching frequency (or BO asymmetric stretching frequency, in the dialkoxyborazens). To select a second band as arising from the corresponding BN mode, would be speculative, and the appearance of doublets, of appropriate frequency separations and relative intensities expected from the $^{11}B/^{10}B$ isotopic effect, cannot be regarded as conclusive. Thus, whereas the majority of the compounds had bands at ~1500 cm.$^{-1}$, with weaker ones at slightly higher frequency, this feature also appears in many organic boron compounds which do not contain nitrogen [*e.g.*, di-n-butyl chloroboronate, $(Bu^nO)_2B{\cdot}Cl$, has a doublet in this region (1493 and 1504 cm.$^{-1}$) [4]]. It is, therefore, likely that the doublet near 1500 cm.$^{-1}$ arises from CH deformation and this value, rather higher than usual, may be attributed to the fact that the CH group is attached through an oxygen or nitrogen atom to the electronegative boron.

CN *Asymmetric Stretching Frequencies.*—In aliphatic amines, the CN (asymmetric) stretching vibration is believed to lie in the 1220—1020 cm.$^{-1}$ region,[10] but only for the methylamines has a detailed treatment of the spectra been made; a band at ~1040 cm.$^{-1}$ was assigned to the CN stretching mode and one at ~1150 cm.$^{-1}$ to a CH_3 wagging mode.[11] In higher secondary aliphatic amines, a band of medium intensity at ~1040 cm.$^{-1}$ persists, but a stronger band at 1130—1170 cm.$^{-1}$ was designated as the asymmetric CN stretching frequency.[12] In aromatic amines, the CN absorption falls at higher frequency (1250—1360 cm.$^{-1}$), which is consistent with there being a higher CN bond order in aromatic than in aliphatic amines.[13] However, it appears that this band does not arise solely from the CN stretching mode, but is coupled with the NH deformation.

TABLE 2. *The trisalkylaminoborons.*

R in $B(NHR)_3$	Me	Et	Pr^i	Bu^n	Bu^s	Bu^t	Cyclohexyl	$Ph{\cdot}CH_2$	Ph
ν_{NH} * (cm.$^{-1}$) ...	3420	3436	3422	3425	3460	3430	3425	3448	3390
ν_{BN} † (cm.$^{-1}$) ...	1499	1502	1493	1499	1496	1490	1493	1498	1510
ν_{CN} † (cm.$^{-1}$) ...	1139	1145	1117	1139	1166	1190	1143	?	1314

* The results show accuracy of ±10 cm.$^{-1}$.
† The results show accuracy of ±2 cm.$^{-1}$.

TABLE 3. BO *Stretching frequencies in alkoxyborazens.*

Compound	$(Bu^nO)_2B{\cdot}NEt_2$	$(Bu^nO)_2B{\cdot}NBu^n_2$	$(Bu^nO)_2B{\cdot}NHEt$	$Bu^nO{\cdot}B(NEt_2)_2$
ν_{BO} (cm.$^{-1}$) (±2 cm.$^{-1}$) ...	1333	1333	1335	1269
Compound	$Bu^nO{\cdot}B(NBu^n{}_2)_2$	$Bu^nO{\cdot}B(Cl){\cdot}NMe_2$	$Bu^nO{\cdot}B(Cl){\cdot}NEt_2$	
ν_{BO} (cm.$^{-1}$) (±2 cm.$^{-1}$) ...	1269	1280	1294	

From the spectrum of trismethylaminoboron, one could select either a strong band at 1139 or a weaker one at 1021 cm.$^{-1}$ as arising from the CN stretching vibration, with the other as the CH_3 wagging mode. In the spectra of higher homologues, the wagging mode would be expected to shift to lower frequencies, whilst the CN band would probably be fairly constant in position. In fact, a band at ~1020 cm.$^{-1}$ appears only for trisdiethylaminoboron (at 1047 cm.$^{-1}$), but not in higher homologues. We therefore prefer to assign

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[10] Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen, London, 2nd edn., 1958, p. 258.
[11] Barceló and Bellanato, *Spectrochim. Acta*, 1956, **8**, 27.
[12] Hadži and Skrbljak, *J.*, 1957, 843.
[13] Brown, *Acta Cryst.*, 1949, **2**, 228; 1951, **4**, 100.

the 1139 cm.$^{-1}$ band in trismethylaminoboron to the CN stretching mode and correspondingly at 1145 (Et), 1117 (Pr^i), 1139 (Bu^n), 1166 (Bu^s), and 1190 (Bu^t) cm.$^{-1}$ in the higher trisalkylaminoborons. It is relevant that in *N*-methylacetamide (where the CH_3·NH group is also attached to an electronegative substituent),[14] the CH_3–N stretching mode was considered to make an 80% contribution to a band at 1069 cm.$^{-1}$ and the CH_3·N wagging mode was located at 1042 cm.$^{-1}$.

In the spectrum of trisphenylaminoboron, there are only three bands in the 1685—1150 cm.$^{-1}$ region which are not definitely associated with aromatic or NH vibrations; and these are at 1510vs, 1314m (with shoulder at 1300), and 1265wm cm.$^{-1}$. The strongest of these we have already assigned to the BN vibration, and one of the remaining ones must arise from the CN mode and, on intensity grounds, the 1314 cm.$^{-1}$ is the more likely although there may well be some contribution from other modes, particularly NH deformation. It is noteworthy that *N*-phenylacetamide [9] also has bands at 1326 and 1266 cm.$^{-1}$ and that the *N*-alkylanilines [12] have the CN absorption at 1240—1260 cm.$^{-1}$.

In the trisdialkylaminoborons, $B(NR_2)_3$, the situation is less clear, but Becher [6] has assigned a band at 1195 cm.$^{-1}$ ($R_2 = Me_2$) to the NC_2 asymmetric stretching vibration and, by analogy, comparable bands are found at 1199 ($R_2 = Et_2$), 1212 ($R_2 = Bu^n{}_2$), and 1216 ($R_2 = C_5H_{10}$) cm.$^{-1}$ in higher homologues. In the alkoxyborazens, corresponding bands appear at 1170—1185 cm.$^{-1}$.

In *N*-alkylanilines, two strong bands have been observed, at 1262 (assigned to aromatic CN) and 1060 cm.$^{-1}$ (assigned to aliphatic CN).[12] It is to be expected, therefore, that similar bands would appear for trismethylphenylaminoboron and these are indeed found at 1285 and 1106 cm.$^{-1}$.

Further Examination of Spectra of Representative Compounds.—We have selected the spectra of trismethylaminoboron, trisphenylaminoboron, trimethylphenylamino)boron, and trisdimethylaminoboron for more detailed assignment, because these compounds are the lowest homologues in the four series $B(NHR)_3$, $B(NHAr)_3$, $B(NRAr)_3$, and $B(NR_2)_3$. The last of these has been described and discussed by Becher,[6] and our observations are in agreement (within 5 cm.$^{-1}$ for each band), though we differ on the assignment of the BN asymmetric stretching frequency (see p. 5240). The spectra of the three remaining compounds are reproduced in Figs. 2—4 and of trisdi-n-butylaminoboron in Fig. 1; assignments are detailed in Table 1.

The spectra of trismethylaminoboron and tri(di-n-butylamino)boron call for no further comment, but in that of trisphenylaminoboron there are bands at 1314 and 1218 cm.$^{-1}$ which we have left unassigned. The latter is likely to be due to the mass-dependent A_1-aromatic vibration, which in aniline is at 1270 cm.$^{-1}$ but in dimethyl(phenylamino)boron, Me_2B·NHPh,[7] lies at 1226 cm.$^{-1}$. The 1314 cm.$^{-1}$ band corresponds in position and intensity to one at 1315 cm.$^{-1}$ in dimethyl(phenylamino)boron (which, however, was assigned to a CH_3 bending mode) [7] and to one at 1326 cm.$^{-1}$ in *N*-phenylacetamide.[9]

In the tri(methylphenylamino)boron spectrum, complete assignment is possible, except for bands at 1475 (absorption is in part or wholly due to CH deformation), 1203, 1122, and 1044 cm.$^{-1}$. The second may well arise from the mass-dependent A_1-aromatic vibration and the last may be due to CH_3 wagging.

DISCUSSION

The BN *Asymmetric Stretching Vibration.*—The values for trisalkylaminoborons, $B(NHR)_3$, are at higher frequencies than for trisdialkylaminoborons, $B(NR_2)_3$, and this is reflected also in the position of the CN stretching frequencies (which are higher in the latter class of compound). It is concluded, therefore, that the BN bond order in the former is greater than in the latter, *i.e.*, that contributions of structures of type (I) are relatively more important than those of type (II), for the two classes respectively. This is

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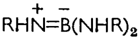
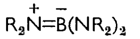
[14] Miyazawa, Shimanouchi, and Mizushima, *J. Chem. Phys.*, 1958, **29**, 611.

contrary to the expectation that inductive and/or hyperconjugative electron-release of the additional alkyl group in the dialkyl derivatives would assist double bonding between nitrogen and boron. With the monoalkyl compounds, structures of type (III) are therefore probably significant. In support of this argument, we note that the BO asymmetric stretching frequency for boric acid [15] (1450 cm.$^{-1}$) is higher than for boric esters [8] (~1350 cm.$^{-1}$) and likewise is higher for phenylboronic acid (1365 cm.$^{-1}$) than for phenylboronates (1330 ± 10 cm.$^{-1}$).[4,16] An alternative, or additional, explanation is that substitution of a hydrogen atom on the nitrogen (or oxygen) atom by an alkyl or aryl group increases the steric strain in the BN (or BO) bond, with consequent bond lengthening.[17] It may therefore be relevant that the lowest value for the BN stretching frequency was observed in tri(methylphenylamino)boron. The proposition that the BN bond order in the trisalkylaminoborons is higher than in the dialkylamino-analogues and is lowest in tri(methylphenylamino)boron receives support from some recent chemical observations.[17] Thus, a primary amine displaces a secondary amine from a trisdialkylaminoboron and is itself displaced from a trisalkylaminoboron by ammonia; tri(methylphenylamino)boron is so far unique amongst borazens [although other compounds $B(NRAr)_3$ will no doubt be found to behave similarly] in being resistant to attack by water or other nucleophilic reagents.

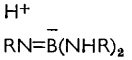
The above argument, equating changes in BN frequencies with changes in bond order, neglects mass effects of different substituents on the nitrogen atom on the BN stretching frequency. However, such effects would be very small; this is borne out by examination of values for BN stretching frequencies within any one homologous series (*e.g.*, see Table 2), which appear to be virtually mass-independent.


$\overset{+}{\mathrm{RHN}}=\overset{-}{\mathrm{B}}(\mathrm{NHR})_2$

(I)


$\overset{+}{\mathrm{R_2N}}=\overset{-}{\mathrm{B}}(\mathrm{NR_2})_2$

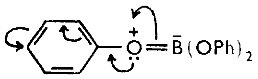
(II)


$\overset{\mathrm{H}^+}{\mathrm{RN}}=\overset{-}{\mathrm{B}}(\mathrm{NHR})_2$

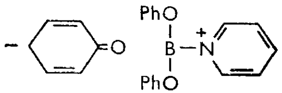
(III)

That the BN asymmetric stretching vibration in borazens is at considerably higher frequency than the corresponding BO mode in boric esters indicates that the degree of p_π–p_π-overlap is greater in the former compounds. This agrees with an earlier thermochemical and theoretical treatment [18] and with some spectroscopic observations on amino-derivatives of ethylene- and *o*-phenylene-boric acid.[19] Also, the relative constancy of the BN frequency in the various compounds indicates a multiple- rather than a single-bond order.

In the trisalkylaminoborons, the position of the BN stretching absorption is remarkably insensitive to variations in the nature of the alkyl group, whilst for the phenyl compound a slightly higher value is found. This is exactly paralleled by the situation in the trialkyl and triphenyl borates. It appears likely, therefore, that structures of type (I) are relatively more important for R = Ph, because of stabilisation resulting from delocalisation of



(IV)



(V)

the positive charge; and similarly for boric esters the BO bond order is highest for triaryl borates. This is in some ways a surprising conclusion, because it has previously been shown that triaryl borates are better electron-pair acceptors than trialkyl borates; *e.g.*, triphenyl borate, unlike trialkyl borates [except tris-(1,1,1-trifluoroethyl) borate], forms

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[15] Bethell and Sheppard, *Trans. Faraday Soc.*, 1955, **51**, 9.
[16] Dandegaonker, Gerrard, and Lappert, *J.*, 1957, 2872.
[17] Aubrey and Lappert, *Proc. Chem. Soc.*, 1960, 148.
[18] Skinner and Smith, *J.*, 1954, 3930.
[19] Blau, Gerrard, Lappert, Mountfield, and Pyszora, *J.*, 1960, 380.

a stable complex with pyridine.[20] However, these observations can be reconciled with the present view and are taken as providing a new example of the polarisability of the phenyl group. Attack by pyridine on the boron atom of triphenyl borate may thus be regarded as bringing into play an electromeric effect in the BO bond [see (IV)] and the resulting pyridine complex has the additional possibility of resonance stabilisation by contribution of structures of type (V).

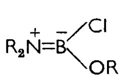
The same situation does not persist in the disubstituted borazens [*i.e.*, ν_{BN}, at 1353 cm.$^{-1}$, in $B(NMePh)_3$ is much lower than in $B(NR_2)_3$] and it is probable than in tri(methylphenylamino)boron there is steric inhibition to mesomerism, preventing coplanarity of the benzene rings with the BN_3 skeleton. Such an effect has been invoked for the *N*-alkylanilines, to account for otherwise anomalous basic strengths;[21] steric hindrance in tri(methylphenylamino)boron has also been demonstrated chemically, as mentioned above.[17]

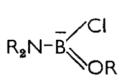
The NH *Stretching Frequency in Trisalkylaminoborons.*—The presence of an electronegative substituent attached to a nitrogen atom in appropriate organic compounds of nitrogen influences the NH vibration and, in general, causes absorption due to the stretching mode at frequencies higher than normal and increases the intensities of both the stretching and bending modes.[22]

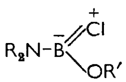
The electronic effect on the nitrogen atom of p_π–p_π-overlap in borazens is analogous to that of a strongly electronegative substituent, and this is borne out by the position of the NH stretching frequencies and by their intensities.

In amines and amides, the position of the NH stretching vibration is sensitive to the state of molecular aggregation; that this is not the case with the borazens indicates that in these compounds intermolecular hydrogen-bonding is either very weak or absent. This is again consistent with there being appreciable double-bond character in the BN bond [cf. (I) and (II)], thus making the nitrogen atoms insufficiently basic to permit hydrogen-bonding.

Aromatic Absorptions in Aromatic Borazens.—Aromatic compounds invariably have a strong band in the 1600 cm.$^{-1}$ region, due to the aromatic CC stretching (A_1) vibration. This band may be accompanied by one of very much lower intensity (B_1) at ~20 cm.$^{-1}$ lower. The second band is generally barely distinguishable, unless the aromatic ring has an unsaturated side chain which allows extended conjugation.[23] The clear separation of the two bands in the aromatic borazens thus provides further independent evidence of multiple bonding between nitrogen and boron; it is noteworthy that in the spectrum of another aromatic borazen, $Me_2B{\cdot}NHPh$,[7] the same feature may be observed.


(VI)


(VII)


(VIII)

BO *Stretching Frequencies in Alkoxyborazens.*—The availability of lone pairs of electrons, not only on nitrogen but also on oxygen and chlorine, in the compounds listed in Table 3, makes it possible that structures of types (VI)—(VIII) in the alkoxychloroborazens (taken as examples) could be contributing canonical forms.

It has already been indicated (see p. 5244 and refs. 18 and 19) that the p_π–p_π-overlap order is N > O > Cl, with respect to boron, and it is therefore to be expected that this would be reflected in the relative importance [(VI) > (VII) > (VIII)] of the above structures. This leads to the conclusion that the BN bond orders, and hence BN

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[20] Colclough, Gerrard, and Lappert, *J.*, 1955, 907; Abel, Gerrard, Lappert, and Shafferman, *J.*, 1958, 2895.

[21] Baddeley, Chadwick, and Taylor, *J.*, 1954, 2405.

[22] Ref. 10, pp. 205, 249; Barr and Haszeldine, *J.*, 1955, 4169.

[23] Ref. 10, pp. 71, 73.

(asymmetric) stretching frequencies, should increase in the series: (i) $B(NR_2)_3 <$ $Cl{\cdot}B(NR_2)_2 < Cl_2B{\cdot}NR_2$; (ii) $B(NR_2)_3 < R'O{\cdot}B(NR_2)_2 < (R'O)_2B{\cdot}NR_2$; and (iii) $B(NR_2)_3 < (R'O)_2B{\cdot}NR_2 < R'O{\cdot}B(Cl){\cdot}NR_2$. This is not easy to verify, because of the difficulty of making definite assignments for the BN stretching vibration in the substituted borazens. However, by similar argument, the fact that the BO (asymmetric) stretching frequency increases in the series: (iv) $R'O{\cdot}B(NR_2)_2 < (R'O)_2B{\cdot}NR_2 < B(OR')_3$ [see Table 3; ν_{BO} in $B(OBu^n)_3$ [8] at 1336 cm.$^{-1}$]; and (v) $R'O{\cdot}B(NR_2)_2 < R'O{\cdot}BCl{\cdot}BR_2$ (see Table 3) shows that N > O and N > Cl as donor to boron. The order O > Cl may likewise be derived from: (vi) $B(OR)_3$ [8] $< Cl{\cdot}B(OR)_2$.[24]

Experimental.—The compounds were prepared and purified as described in previous papers [$B(NHR)_3$,[25] $B(NR_2)_2$,[26,27] and alkoxyborazens [25,26]].

The spectra were measured in a Grubb–Parsons S.3A double-beam spectrometer, fitted with sodium chloride optics. The instrument was calibrated throughout its range by means of accepted primary standards (ammonia, carbon dioxide, and water). Samples were studied as liquid capillary films, or [R in $B(NHR)_3$ = cyclohexyl, Ph, or CH_2Ph; and R_2 in $B(NR_2)_3$ = Me and Ph, or pentamethylene] as solid mulls in paraffin oil, as appropriate. Trisethylaminoboron and triscyclohexylaminoboron were also investigated as solutions in CCl_4.

As the spectra have been submitted for reproduction in the D.M.S. punched-card system, only relevant portions have been discussed.

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[24] Lehmann, Onak, and Shapiro, *J. Phys. Chem.*, 1959, **30**, 1219.
[25] Lappert, *Proc. Chem. Soc.*, 1959, 59; Aubrey and Lappert, *J.*, 1959, 2927.
[26] Gerrard, Lappert, and Pearce, *J.*, 1957, 381; *Chem. and Ind.*, 1958, 292.
[27] Aubrey and Lappert, to be published.