Assignment of Vibrational Spectra of some Dialkylamido-derivatives of Boron

By **George Davidson*** and **Stephen Phillips**, Department of Chemistry, University of Nottingham, Nottingham NG7 2RD

A number of inconsistencies and errors in previous vibrational assignments for molecules containing B–NR$_2$ groups have been corrected. This was achieved by studying the i.r. and Raman spectra of B(NR$_2$)$_3$, B[N(CH$_2$)$_4$]$_3$, B(NR$_2$)$_2$Br, and B$_2$(NR$_2$)$_4$, where R = Me or Et. The antisymmetric BN stretches were always above 1 500 cm^{-1}, with the symmetric BN stretches near 1 350 cm^{-1}. The value of ν(B–B) in the diboron compounds was *ca.* 1 230 cm^{-1}. In B(NR$_2$)$_3$ there is extensive vibrational coupling between the NR$_2$ groups.

WE have recently reported the assignment of vibrational wavenumbers for E(NR$_2$)$_3$, where E = P or As; R = Me or Et.[1] It was interesting to extend this work to analogous compounds containing boron instead of phosphorus or arsenic. The known tendency of B–N bonds to possess double-bond character might be expected to alter significantly the vibrational spectra.

A number of vibrational studies of dialkylamido-compounds of boron have been made,[2–8] but a close study of these revealed that the vibrational assignments were incomplete or contradictory. The two chief contradictions concerned the B–N stretching wavenumber in B(NR$_2$)$_3$, and the B–B stretching wavenumber in B$_2$(NR$_2$)$_4$. The former was assigned [3] to 607 cm^{-1} (ν_{sym} BN$_3$) and 1 379—1 393 cm^{-1} (ν_{asym} BN$_3$; ^{10}B–^{11}B isotopic splitting). The B–B stretch in B$_2$(NMe$_2$)$_4$ was assigned to a value of *ca.* 580 cm^{-1}. These should be compared with B–N stretching wavenumbers of 1 370 cm^{-1} (ν_{sym} BN$_2$) and 1 532—1 555 cm^{-1} (ν_{asym} BN$_2$, ^{11}B–^{10}B) in B(NMe$_2$)$_2$Cl,[7] and ν(BB) for B$_2$Cl$_4$·2PH$_3$ (1 061 cm^{-1}).[9] In addition, few detailed assignments were proposed for the internal NR$_2$ modes.

In order to remove these inconsistencies, and to obtain a valid comparison between the vibrational spectra of the boron and the phosphorus or arsenic dialkylamides, we have recorded and assigned the i.r. and Raman spectra of B(NR$_2$)$_3$, B[N(CH$_2$)$_4$]$_3$, B(NR$_2$)Br, and B$_2$(NR$_2$)$_4$, where R = Me or Et.

RESULTS

The observed i.r. and Raman spectra for the compounds studied are listed in Supplementary Publication No. SUP 22937 (15 pp.),† together with a summary of the proposed assignments. The assignments of the most important modes are given in Tables 1—4, see the discussion below.

DISCUSSION

(i) *Vibrational Analyses.*—The molecular structure of B(NMe$_2$)$_3$ in the vapour phase has been determined by electron diffraction.[10] The BN$_3$ unit and the three BNC$_2$ units are all planar, but the dimethylamido-groups are twisted by approximately 30° out of the BN$_3$ plane, giving an overall molecular symmetry of D_3. It is reasonable to suppose that this symmetry will persist in the liquid phase, and so for B(NMe$_2$)$_3$ a symmetry of D_3 will be used as the basis for the assignment.

The numbers and symmetry types of the vibrational modes for B(NMe$_2$)$_3$ will therefore be as follows: (a) BN$_3$ stretch: $A_1 + E$; (b) BN$_3$ in-plane deformation: E; (c) BN$_3$ out-of-plane deformation: A_2; (d) NC$_2$ stretch: $A_1 + A_2 + 2E$; (e) BNC$_2$ in-plane deformation: $A_1 + A_2 + 2E$; (f) BNC$_2$ out-of-plane deformation: $A_1 + A_2 + 2E$; (g) CH$_3$ stretch: $3A_1 + 3A_1 + 6E$; (h) CH$_3$ deformation: $5A_1 + 5A_2 + 10E$; and (i) CH$_3$ torsion: $A_1 + A_2 + 2E$. The selection rules for D_3 symmetry predict the following spectroscopic activity: A_1, Raman only (polarised); A_2, i.r. only; E, i.r. and Raman (depolarised).

The predicted numbers of modes for the internal vibrations of the NMe$_2$ units given above will apply if there is significant vibrational coupling between the units. If they vibrate independently, then it is possible to use a 'local symmetry' approach, with C_{2v} symmetry for an effectively isolated NMe$_2$ group. This would result in the appearance of fewer bands, *e.g.* for the CH$_3$ stretches one would then only expect to see six bands ($2A_1 + A_2 + B_1 + 2B_2$), all Raman active (two polarised) and five i.r. active. This should be compared with the nine Raman bands (three polarised) and nine i.r. bands (three not coincident with Raman features) predicted by the D_3 model. For P(NMe$_2$)$_3$ and As(NMe$_2$)$_3$ the 'local symmetry' approximation was sufficient, but with extensive delocalised π bonding expected in the BN$_3$ skeleton it is less likely to apply for B(NMe$_2$)$_3$.

For the more complex tris(dialkylamido)boranes we will not attempt such a detailed assignment of the vibrations for the ethyl groups or the methylene rings in B(NEt$_2$)$_3$ and B[N(CH$_2$)$_4$]$_3$ respectively. Skeletal modes, of B(NC$_2$)$_3$, will again be assigned assuming D_3 symmetry.

The molecular symmetry of B(NMe$_2$)$_2$Br will be C_{2v}, and it is also expected that vibrations of the B(NC$_2$)$_2$Br skeleton of the ethyl analogue will be assignable under that symmetry.

There have been no structural investigations on B$_2$(NR$_2$)$_4$, where R = Me or Et. The crystal and molecular structure of the cyclic analogue *BB'*-bis(dimethyl-1, 3-diaza-2-boracyclopentane) have been determined, however, showing an overall molecular symmetry of D_2.[11] This symmetry will be assumed for B$_2$(NR$_2$)$_4$, although it is conceivable that the BNC$_2$ planes could be perpendicular to that of B$_2$N$_4$, giving D_{2d} symmetry; an all-

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† For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1979, Index issue.

planar structure (D_{2h}) can be ruled out, as this would require the mutual exclusion rule to be obeyed, which clearly it is not.

As for $B(NMe_2)_3$, so for $B_2(NMe_2)_4$, it will be interesting to see whether there is evidence of coupling between NMe_2 groups.

(ii) *Tris(dimethylamido)borane.*—The highest wavenumber fundamentals are the CH_3 stretches, and it is these which will give the clearest indication as to the extent of coupling between the NMe_2 groups. The assignments will be made by analogy with those for $P(NMe_2)_3$, $As(NMe_2)_3$,[1] and dimethylamine itself.[8]

The first point to notice, in comparison with *e.g.* $P(NMe_2)_3$, is the great complexity of the spectrum in this region. There are certainly more than the six fundamentals predicted for an isolated NMe_2 group, so that there must be significant interaction between the NMe_2 groups. The proposed assignment is given in Table 1.

TABLE 1

Assignment of NMe_2 modes in $B(NMe_2)_3$ (all figures in cm^{-1})

CH_3 stretches	A_1	2 893	CH_3 deformations	A_1	1 488
	A_1	2 841		A_1	1 337
	A_1	2 791		A_1	1 319
	A_2	2 912		A_2	1 498
	A_2	2 830		A_2	1 403
	A_2	2 778		A_2	
	E	2 987		E	1 498
	E	2 934		E	1 466
	E	2 893		E	1 450
	E	2 869		E	1 438
	E	2 841		E	1 411
	E			E	
CH_3 rocks	A_1	1 030	NC_2 stretches	A_1	?1 030
	A_1			A_2	962
	A_2	1 123		E	1 065
	A_2	1 099		E	908
	E	1 222			
	E	1 147	CH_3 torsion	A_1	345
	E	1 108		A_2	310
	E	1 050		$2E$	345

The polarisation properties and spectral activities of all of the bands are consistent with D_3 symmetry, with the exception that the Raman feature at 2 934 cm^{-1}, assigned as an E mode, is weakly polarised. One explanation of this could be the presence of a component due to the first overtone of the methyl deformation at 1 466 cm^{-1}. The only remaining comment to be made concerning the assignment is that we postulate two accidental degeneracies, at 2 893 cm^{-1} ($A_1 + E$) and 2 841 cm^{-1} ($A_1 + E$).

It is convenient to consider all of the methyl internal vibrations before dealing with the skeletal modes. The methyl ' deformations ' can be subdivided into the deformations proper and the CH_3 rocking modes. Table 1 shows that almost complete assignments are possible for all of these modes. It is clear that there are more fundamentals than can be accounted for in terms of an isolated NMe_2 unit (nine distinct wavenumbers for the deformations, seven for the rocks), providing confirmation of the existence of significant vibrational coupling.

The only remaining CH_3 vibrations are the torsions. Here a detailed assignment is impossible, but two bands are seen in the expected region [by analogy with *e.g.* $P(NMe_2)_3$], *i.e.* 310 cm^{-1} (i.r. only, A_2) and 345 cm^{-1} (Raman only, polarised, A_1 + ?2E).

Turning now to the skeletal modes, by analogy with other B–N compounds we believe that the antisymmetric BN_3 stretch is seen at 1 504 cm^{-1} (^{11}B) and 1 518 cm^{-1} (^{10}B), with the symmetric mode at 1 319 cm^{-1} or 1 337 cm^{-1}. The latter are accidentally degenerate with CH_3 deformations. The present assignments are markedly different from those proposed by Becher,[3] but consistent with other assignments for $B-NR_2$ compounds [4-7] and for borazines,[12,13] in which the B–N bond lengths are very similar to that found for $B(NMe_2)_3$.[10] Calculations by Finch *et al.*[8] suggest that the symmetric BN_3 stretch (A_1) could be mixed extensively with symmetric CH_3 deformations.

Assignment of NC_2 stretches and CH_3 rocking modes, see above, to specific bands is not easy, as their wavenumber ranges overlap. Earlier workers have assigned NC_2 stretches over a wide spectral range, *e.g.* in $B(N\text{-}Bu^n{}_2)_3$ and $B(NHMe)_3$, Aubrey *et al.*[14] assigned them at 1 212 and 1 139 cm^{-1} respectively, while Becher,[5] for Me_2BNMe_2, preferred 1 111 and 987 cm^{-1}. Bearing in mind that the NC_2 stretches and the CH_3 rocks will be heavily mixed, and that the descriptions of modes in this region will be very approximate, we give the assignments listed in Table 2. The Raman band at 1 030 cm^{-1} is the only definitely polarised band in this region, and it could be either the A_1 CH_3 rock or the A_1 NC_2 stretch; in $P(NMe_2)_3$ the symmetric NC_2 stretches are below 1 000 cm^{-1}, and so the 1 030 cm^{-1} band is more likely to be the CH_3 rock.

By analogy with previous work on planar XY_3 units, we believe that the next mode to be assigned is the BN_3 out-of-plane deformation (A_2). In BF_3,[15] $C(NH_2)_3{}^+$,[16] and $C(CH_2)_3$ [17,18] the equivalent mode lies in the range 700—800 cm^{-1}, with the in-plane deformation at lower wavenumbers (450—520 cm^{-1}). In $B(NMe_2)_3$ an i.r.-only band at 714 cm^{-1} is an obvious candidate for the out-of-

TABLE 2

Assignments of $B(NC_2)_3$ modes in $B(NR_2)_3$, where R = Me or Et, or $R_2 = (CH_2)_4$ (all figures in cm^{-1})*

		R = Me	R = Et	$R_2 = (CH_2)_1$
BN_3 stretch	A_1	1 337/ 1 319	1 347	1 298
	E	1 518/ 1 504	1 518	1 525/ 1 496
NC_2 stretch	A_1	?1 030	933	see text
	A_2	962	924	
	E	1 065	1 076 or 1 060	
	E	908	924	
BNC_2 i.p. def.	A_1	604	626	
	A_2	686	679	
	E	359	388	
	E	276	311	
BNC_2 o.o.p. def.	A_1	630	?	
	A_2	660	679	
	E	252	146	
	E	161	126	
BN_3 i.p. def.	E	492	472	435
BN_3 o.o.p. def.	A_2	714	707	720

* i.p. def. = In-plane deformation, o.o.p def. = out-of-plane deformation.

plane mode, with the in-plane deformation at 492 cm^{-1} (Raman-only, depolarised).

All of the remaining skeletal modes can be described as in-plane or out-of-plane BNC_2 deformations. Two i.r.-only bands, at 686 and 660 cm^{-1}, are A_2 modes, but no distinction can be made between in- and out-of-plane. An extremely strong, polarised Raman band at 604 cm^{-1} is assigned as the symmetric in-plane BNC_2 deformation (' NC_2 scissors ') of A_1 symmetry. Becher reported[3] a coincident i.r. absorption, contrary to the predictions of D_3 symmetry. Our experiments revealed that such an i.r. band only appeared if the sample had been held for long periods in the spectrometer. It was, therefore, due to a decomposition product.

The remaining assignments are summarised in Table 2. The two lowest-wavenumber features, at 252 and 161 cm^{-1}, can be described more accurately as an NC_2 wag and an NC_2 torsion respectively.

Thus we have achieved a reasonably complete vibrational assignment for $B(NMe_2)_3$, removing inconsistencies in previous assignments of skeletal modes, giving a more detailed assignment than hitherto of the NMe_2 modes, and revealing the existence of significant vibrational coupling between the NMe_2 units.

(iii) *Tris(diethylamido)borane.*—The increased complexity of the spectrum makes a detailed assignment much more difficult, especially for the NEt_2 internal modes. Tentative assignments are given in the Supplementary Publication for these, which will not be discussed further. Table 2, in addition to the results for $B(NMe_2)_3$, also summarises the proposed skeletal assignments for $B(NEt_2)_3$.

The BN_3 stretches are very close to those in $B(NMe_2)_3$ (the slightly higher values for the ethyl compound can be explained by coupling with CH_2 deformation modes), but it was not possible to observe the $^{11}B-^{10}B$ isotopic splitting. The NC_2 stretches are in the same region as in $B(NMe_2)_3$ but in this case the A_1 mode was seen, at 933 cm^{-1}. Where they can be assigned, the skeletal deformations are at very similar wavenumbers to those in the methyl compound.

(iv) *Tris(pyrrolidino)borane.*—A detailed vibrational analysis of free pyrrolidine has been carried out by Evans and Wahr[19] and this has been used to assign the corresponding modes here. They are summarised in the Supplementary Publication. Some of the skeletal modes are also listed in Table 2, but in this case the NC_2 stretches and the BNC_2 deformations will have become vibrations of the cyclic ligands, and cannot be assigned in the same way as for the other molecules.

The BN_3 stretches can be assigned to features in the same regions as in the $B(NR_2)_3$ molecules already described. The symmetric mode, of A_1 symmetry, at 1 298 cm^{-1}, however, shows an i.r. band coincident with the polarised Raman band. This may indicate a breakdown in D_3 symmetry for the tris(pyrrolidino)-derivative, although there are a number of CH_2 deformation modes in this region of the spectrum, and a plausible explanation of the i.r. band may be that is is an A_2 component of the CH_2 twist, accidentally degenerate with the symmetric BN_3 stretch.

At lower wavenumbers, although the internal pyrrolidino-vibrations give a complicated spectrum, there are i.r. bands in the regions expected for BN_3 in-plane and out-of-plane deformations, at 435 and 707 cm^{-1} respectively.

(v) *Bromobis(dialkylamido)boranes.*—Quite detailed assignments have been proposed for $B(NMe_2)_2Cl$.[7] We will discuss the bromo-analogue, and the NEt_2 derivatives rather briefly, however, as some of our skeletal mode assignments differ from those for the chloro-compound, for which the Raman polarisation data were very incomplete.

The N_2BBr unit is expected to be planar, and the overall symmetry of the methyl compound will be C_{2v} if the BNC_2 units are coplanar with the N_2BBr plane, and C_2 if they are not. The assignment which we propose is consistent with C_{2v} symmetry. We will concentrate upon the assignments for the methyl compound, as the Raman data for the ethyl compound were much less complete, due to sample fluorescence.

The internal modes of the alkyl groups are all in the expected regions, and the assignments are summarised in the Tables in the Supplementary Publication. In both cases there were more bands than could be explained by an isolated NR_2 unit but the extent of vibrational coupling appeared to be less than for $B(NR_2)_3$, as less bands were resolvable.

The skeletal mode assignments are given in Table 3.

TABLE 3

Assignments of $B(NC_2)_2Br$ modes in $B(NR_2)_2Br$, where R = Me or Et (all figures in cm^{-1})*

		R = Me	R = Et
A_1	BN_2 stretch	1 349	1 338
	NC_2 stretch	921	985
	NC_2 stretch	869	868
	BNC_2 i.p. def.	605	597
	BNC_2 i.p. def.	562	580
	BBr stretch	331	361
	N_2BBr i.p. def.	270	
A_2	BNC_2 o.o.p. def.	241	?411
	N_2BBr o.o.p. def.	219 or 117	289
B_1	BN_2 stretch	1 532—1 555	1 519—1 543
	NC_2 stretch	1 064	1 078
	NC_2 stretch	893	922
	BNC_2 i.p. def.	589	566
	BNC_2 i.p. def.	496	499
	N_2BBr i.p. def.	458	468
B_2	BNC_2 o.o.p. def.	404	398
	BNC_2 o.o.p. def.	186	?
	N_2BBr o.o.p. def.	117 or 219	?

* See footnote to Table 2.

In both compounds the antisymmetric BN_2 stretches gave clear ^{11}B and ^{10}B components, separated by over 20 cm^{-1}, at 1 532 and 1 555 cm^{-1} for $B(NMe_2)_2Br$. The symmetric BN_2 stretch in $B(NMe_2)_2Br$ was assigned as being accidentally degenerate with a CH_3 deformation at 1 349 cm^{-1}, while in the ethyl compound it gave a separate (i.r.) band at 1 338 cm^{-1}.

Our assignments of NC_2 stretches are in the same region as those of Goubeau *et al.*[7] for $B(NMe_2)_2Cl$, except that the band near 1 075 cm^{-1} in the latter (assigned earlier as an A_1 mode) corresponds to a depolarised feature at 1 061 cm^{-1} in $B(NMe_2)_2Br$. This is, therefore, assigned as an antisymmetric mode (B_1), with the A_1 modes at lower wavenumbers. Due to vibrational mixing of modes involving the NC_2 stretches and CH_3 rocks (in the methyl compound) or CH_2 deformations (in the ethyl compound) the positions of the features assigned as NC_2 stretches are somewhat different in the two compounds, as shown in Table 3.

The remaining skeletal vibrations are BNC_2 deformations (in-plane, $2A_1 + 2B_1$; out-of-plane, $A_2 + 2B_2$), N_2BBr deformations (in-plane, $A_1 + B_1$; out-of-plane, $A_2 + B_2$), and the BBr stretch (A_1). Goubeau *et al.*[7] assigned in-plane BNC_2 deformations in the range 300—400 cm^{-1}, but our values for $B(NR_2)_3$ are between 580 and 680 cm^{-1}, and we feel that the latter region is more appropriate here also. A weak, polarised Raman band at 605 cm^{-1} is assigned as one in-plane BNC_2 deformation, with the other, the ' NC_2 scissors ' mode, as the very strong, polarised Raman band at 562 cm^{-1} (both had i.r. counterparts). The two antisymmetric (B_1) modes are at 589 cm^{-1} (i.r. only) and 496 cm^{-1} (i.r. and Raman depolarised).

The out-of-plane BNC_2 deformations are at 404 cm^{-1} (i.r. only, B_2), 241 cm^{-1} (Raman, A_2, NC_2 wag), and 186 cm^{-1} (Raman, B_2, NC_2 twist). The last two are very close to the values in $B(NMe_2)_3$.

The BBr stretch would be expected to give a strong, polarised Raman band, and it is assigned to that at 331 cm^{-1}. This is consistent with the assignments of symmetric modes with BBr stretching character in BX_2Br (X = F, Cl, or I).[20]

An antisymmetric, B_1, in-plane N_2BBr deformation is thought to give rise to the weak, depolarised Raman band at 458 cm^{-1}, while the symmetric mode, A_1, gives a polarised band at 270 cm^{-1}. The remaining skeletal deformations, out-of-plane N_2BBr deformations, give depolarised Raman bands at 219 and 117 cm^{-1}, but it is not possible to differentiate between the A_2 and B_2 modes in the absence of far-i.r. data.

The assignments of low-wavenumber skeletal modes in $B(NEt_2)_2Br$ are broadly in agreement with those for $B(NMe_2)_2Br$, but are very incomplete.

(vi) *Tetrakis(dialkylamido)diboranes*.—Crystallographic results on related compounds, and previous vibrational assignments (Becher *et al.*,[4] Finch *et al.*[8]), all suggest that the effective molecular symmetry is D_2. There are significant gaps in the published vibrational studies, which also include some doubtful assignments. Chief among these are the placing of the highest wavenumber BN_2 stretch at *ca.* 1 400 cm^{-1} (contrary to many other assignments, and those discussed above), and of the B–B stretch near 580 cm^{-1}. The latter should be compared with the B–B stretching wavenumbers in the diboron tetrahalides B_2X_4, X = F, 1 404 cm^{-1},[21] Cl, 1 122 cm^{-1},[22] I, 1 076 cm^{-1}.[23]

We will consider in detail only the methyl compound. In this case the ethyl groups lead to great complexity in the spectrum, and specific assignments are very difficult. Further, attention will be focused on the skeletal modes, *i.e.* those involving $B_2(NC_2)_4$. The alkyl internal modes can be assigned in general terms, and are indicated in the Tables in the Supplementary Publication. They show that vibrational coupling between the alkyl groups on different NR_2 groups is slight.

Skeletal modes for the methyl compound are listed in Table 4. In D_2 symmetry it is impossible, with the data available, to differentiate between B_1, B_2, and B_3 modes, hence, the only distinction made is between A and ' B ' modes.

TABLE 4

Assignments of $B_2(NC_2)_4$ modes in $B_2(NMe_2)_4$ (all figures in cm^{-1})

A	B_2N_4 stretch	1 369	*A*	BN_2 scissors	709
	BB stretch	1 236		NC_2 scissors	578
	NC_2 stretch	1 100		NC_2 rock	375
	NC_2 stretch	967		NC_2 wag	261
	BN_2 twist	786		NC_2 twist	246
B	B_2N_4 stretch	1 525—1 547	*B*	NC_2 scissors	615
	B_2N_4 stretch	1 503—1 508		NC_2 rock	565
	B_2N_4 stretch	1 337		NC_2 rock	364
	NC_2 stretch	1 061		NC_2 rock	?
	NC_2 stretch	1 049		BN_2 wag	549
	NC_2 stretch	1 018		BN_2 wag	454
	NC_2 stretch	889		BN_2 rock	320
	NC_2 stretch	837		BN_2 rock	320
	NC_2 stretch	829		NC_2 twist	143
	BN_2 scissors	694		NC_2 twist	143
	NC_2 scissors	641		NC_2 twist	143
	NC_2 scissors	629		NC_2 wags (3)	?

Previous assignment [4,8] of an antisymmetric BN_2 mode to 1 412 cm^{-1} is extremely unlikely, and we prefer to place the two modes (in-phase and out-of-phase BN_2 antisymmetric stretches) as the two ^{11}B–^{10}B doublets at 1 525—1 547 cm^{-1} and 1 503—1 508 cm^{-1}, both i.r. only. The splitting between these two doublets is a measure of the vibrational coupling between the two BN_2 units.

As such coupling occurs, we expect two bands derived from the BN_2 symmetric stretch (in-phase, A, and out-of-phase, B). These can be assigned to the polarised Raman band at 1 337 cm^{-1}, and the depolarised Raman band at 1 369 cm^{-1} respectively. Both have weak i.r. counterparts, even though A modes are i.r. forbidden. This could indicate a slight breakdown in D_2 symmetry or, more likely, accidental degeneracy with a methyl deformation mode.

By analogy with diboron tetrahalides, the next fundamental should be ν(B–B). Careful comparison between the spectra of $B_2(NMe_2)_4$ and $B(NMe_2)_2Br$ shows that the former contains a polarised Raman band at 1 236 cm^{-1} which is absent from the latter. This is assigned to ν(B–B) in preference to the figure of 580 cm^{-1} quoted previously.[4,8] We will discuss below an alternative assignment for the latter band.

The NC_2 stretches will be mixed extensively with methyl rocks, and so assignments can only be tentative. The figures given in Table 4 are, however, consistent with those in related compounds.

A weak, polarised Raman band, with no corresponding i.r. feature, at 786 cm^{-1} is assigned as the BN_2 twist (A

symmetry). As with ν(B–B) this is absent from the spectrum of $B(NMe_2)_2Br$, where this motion corresponds to a molecular rotation.

A further polarised Raman band at 709 cm^{-1} is thought to be the symmetric BN_2 scissors, while the antisymmetric analogue is at 694 cm^{-1}, i.r. only. NC_2 scissors vibrations occur at slightly lower wavenumber; features at 641, 629, and 615 cm^{-1} are the modes of B symmetry, while the symmetric mode gives an extremely strong Raman band, polarised, at 578 cm^{-1}. This was previously assigned as ν(B–B), but the spectra of $B(NR_2)_3$ and $B(NR_2)_2Br$ contain very similar features.

Depolarised Raman bands at 549 and 454 cm^{-1} are assigned as BN_2 wags, while only one feature, a depolarised Raman band at 230 cm^{-1} (i.r. at 318 cm^{-1}) can be assigned as BN_2 rocks (possibly the two modes expected, $B_1 + B_2$, are accidentally degenerate).

The remaining modes are NC_2 rocks (A at 357 cm^{-1}, two B modes possibly at 565 and 364 cm^{-1}), NC_2 wags (A at 261 cm^{-1}, no B modes detected), and NC_2 twists (A at 246 cm^{-1}, three degenerate B modes at 143 cm^{-1}).

Conclusion.—We have been able to make quite detailed vibrational assignments for $B(NR_2)_3$, $B[N(CH_2)_4]_3$, $B(NR_2)_2Br$, and $B_2(NR_2)_4$, where R = Me or Et. These have been more detailed and based on a larger amount of experimental data than previous studies. The three principal conclusions that can be drawn are as follows: (*i*) the BN_3 or BN_2 stretches are near 1 500 cm^{-1} (antisymmetric) or 1 350 cm^{-1} (symmetric) in all cases, in agreement with the known existence of B–N π bonding in such molecules; (*ii*) the B–B stretch in $B_2(NR_2)_4$ is above 1 200 cm^{-1}, consistent with data on diboron tetrahalides; (*iii*) in $B(NR_2)_3$, but not in the other systems studied, there is extensive vibrational coupling between the NR_2 units, in contrast to the situation for $E(NR_2)_3$, where E = P or As, and R = Me or Et.

EXPERIMENTAL

All preparations were carried out under an atmosphere of pure dry argon, and all solvents were dried by distillation from $Li[AlH_4]$ before use. The amines used were dried over $K[OH]$ and redistilled before use.

The tris(dialkylamido)-derivatives were prepared by the method developed by Purdum and Kaiser,[24] the bis(dialkylamido)-bromides by that of Brotherton *et al.*,[25] and the $B_2(NR_2)_4$ by that described by Nöth and Meister [26] and Brotherton *et al.*[25] Satisfactory C, H, and N analyses were obtained in all cases.

Infrared spectra were obtained using a Perkin-Elmer 521 spectrometer (250—4 000 cm^{-1}). Liquid-film samples were held between AgCl or CsI windows. The spectra were calibrated using known wavenumbers of CH_4, HBr, CO, NH_3, and H_2O. All of the observed wavenumbers are accurate to ±2 cm^{-1} (±5 cm^{-1} for very weak and/or broad features).

A Cary 81 spectrometer, modified by Anaspec Ltd., was used to record the Raman spectra, the excitation source being a Spectra-Physics 164 argon ion laser (power output *ca.* 1 W at both 488.0 and 514.5 nm). Liquid samples were distilled directly into glass capillaries, of approximately 1 mm internal diameter, and polarisation measurements carried out by examining the spectrum with the incident light successively parallel and perpendicular to the axis of a polaroid analyser. Depolarisation ratios obtained were directly proportional to the true values. The spectra were calibrated by comparison with the spectrum of indene, and peak positions were accurate to within ±2 cm^{-1}, or ±5 cm^{-1} for very weak and/or broad features.

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