

# Molecular Structures of Gaseous (Monomethylamino)dimethylborane, Bis(monomethylamino)methylborane and Tris(monomethylamino)borane, $(\text{CH}_3)_{3-n}\text{B}(\text{NHCH}_3)_n$ , $n = 1, 2, 3$ , Studied by Electron Diffraction

ARNE ALMENNINGEN, GRETE GUNDERSEN, MARIT MANGERUD and RAGNHILD SEIP

Department of Chemistry, University of Oslo, Oslo 3, Norway

The molecular structures of the title compounds were studied with main emphasis on effects from variation of the dative  $\pi$ -bonding in the B–N bonds throughout the series  $(\text{CH}_3)_{3-n}\text{B}(\text{NHCH}_3)_n$ ,  $n = 1, 2, 3$ . For  $n=2$  a *syn,anti* periplanar conformation was found to be prevailing and  $C_3$ -symmetry was assumed for  $n=3$ . For  $n=1, 2$  and  $3$ , respectively, the B–N bond length ( $r_a(\text{BN})$ ), the average of the overlapping B–N and N–C bond lengths ( $\bar{r}$ ), and the torsional angle about the B–N bonds ( $\theta(\text{BN})$ ) were found to be  $r_a(\text{BN})$ : 1.397(2), 1.418(2) and 1.439(2) Å;  $\bar{r}$ : 1.427(2), 1.437(2) and 1.446(2) Å; and  $\theta(\text{BN})$ : 8(6), 17(2) and 13(2)°.

The planar or nearly coplanar conformations, and the short B–N bond lengths have been ascribed to effects from  $\pi$ -electron backdonation from the nitrogens to the formally empty  $2p_z$  orbital of the trivalent boron. In fact, the variations of the B–N bond length and the  $\bar{r}$  parameter, are in the direction which may be expected for decreasing  $\pi$ -bond strength in the  $n=1$  to  $n=3$  series.

Simplified valence force fields have been derived and used to calculate vibrational amplitudes and shrinkage corrections.

The molecular structures of gaseous methoxyboranes,  $(\text{CH}_3)_{3-n}\text{B}(\text{OCH}_3)_n$ ,  $n = 1, 2, 3$ , as studied by the electron-diffraction method, have previously been reported.<sup>1,2</sup> The results were discussed with emphasis on conformations and on B–O bond-length variations in relation to varying importance of dative  $\pi$ -bonding, potentially, however, obscured by opposing effects due to  $\sigma$ -bond polarizations.

In this paper we shall report corresponding results for the isoelectronic nitrogen series  $(\text{CH}_3)_{3-n}\text{B}(\text{NHCH}_3)_n$ ,  $n = 1, 2, 3$ , i.e. the (monomethylamino)dimethyl-, bis(monomethylamino)methyl- and tris(monomethylamino)boranes, hereafter referred to as BN1, BN2 and BN3, respectively.

Since nitrogen is less electronegative than oxygen, the effects due to  $\sigma$ -bond polarizations may be of lesser importance in the nitrogen series than for the oxygen analogues. The  $\pi$ -donor capacity of aminogroups are claimed to be superior to that of oxygroups.<sup>3,4</sup> According to these considerations and the results of comparative *ab initio* MO-studies<sup>5</sup> of  $\text{H}_2\text{BOH}$ ,  $\text{HB}(\text{OH})_2$ ,  $\text{B}(\text{OH})_3$ ,  $\text{H}_2\text{BNH}_2$ ,  $\text{BH}(\text{NH}_2)_2$  and  $\text{B}(\text{NH}_2)_3$ , a pronounced bond length elongation is to be expected when the number of strong  $\pi$ -donors is increased for the aminoboranes as compared to the slight or insignificant variation observed for the methoxyboranes.<sup>2</sup>

## EXPERIMENTAL AND DATA PROCESSING

Pure samples of BN1, BN2 and BN3, prepared by reacting bromodimethyl-,<sup>6</sup> dibromomethyl-,<sup>7</sup> and trichloroborane,<sup>8</sup> respectively, with methylamine, were supplied for this investigation by Professor H. Nöth and coworkers at the University of Munich.

Electron-diffraction exposures were made for BN3 using a Balzers' Eldigraph KDG-2.<sup>9</sup> In subsequent data recordings for BN1 and BN2, problems due to charging effects were encountered.

Table 1. Experimental and refinement conditions.

Compounds	B(NHCH <sub>3</sub> ) <sub>3</sub> /BN3	CH <sub>3</sub> B(NHCH <sub>3</sub> ) <sub>2</sub> /BN2	(CH <sub>3</sub> ) <sub>2</sub> BNHCH <sub>3</sub> /BN1	Oslo unit <sup>11</sup>
Electron-diffraction unit	Balzers Eldigraph <sup>10</sup>	Oslo unit <sup>11</sup>	Balzers Eldigraph <sup>10</sup>	Oslo unit <sup>11</sup>
Accelerating potential (kV)	42	35	42	35
Electron wavelength (Å)	0.05852	0.06463	0.05851	0.06463
Photographic plate	Replica 23	Scientia 34B50	Replica 23	Scientia 34B50
Sample temperature (°C)	45	0 to 20	-25	-32
Nozzle temperature (°C)	60	15	20	15
Nozzle-to-plate distances (mm)	500.12	480.71	500.12	480.83
		200.71	250.12	200.83
Exposure times (min)	1½-2½	½	1	½
No. of plates	5	4	3	4
Data interval, Δs (Å <sup>-1</sup> )	0.125	0.125	0.125	0.125
Data range (Å <sup>-1</sup> )	1.750	2.000	1.750	2.000
s (min)	15.000	19.250	15.000	19.250
s (max)	5.00	5.00	5.00	5.00
Weighting scheme <sup>a</sup>	12.00	15.00	12.00	15.00
s <sub>1</sub> (Å <sup>-1</sup> )	0.15	0.15	0.15	0.15
s <sub>2</sub> (Å <sup>-1</sup> )	0.03	0.025	0.03	0.025
w <sub>1</sub> (Å <sup>2</sup> )	1.0	1.0	1.0	1.0
w <sub>2</sub> (Å <sup>2</sup> )				
W				

<sup>a</sup> See Ref. 11 for meaning of the constants. *W* is the relative weight on data from each camera distance which are approximately on the same scale.

For BN2 the displacement of the undiffracted electron beam from the position of the beam stop was so severe that no usable data was obtained. Attempts to record diagrams using the Oslo-apparatus,<sup>10</sup> which features a more flexible line up of the electron beam and the beam stop were successful for both BN2 and BN1. Thus, for BN1 two data sets emerged, both of which were analyzed. The experimental conditions are summarized in Table 1. The electron wavelengths used were calibrated against diffraction patterns of gaseous benzene and the uncertainty is estimated to 0.1%.

The densities of the photographic plates were recorded in intervals of 0.25 mm, while oscillating the plates on an integrating densitometer constructed by A. Almenningen and P. Molin. The data were processed in routine manner,<sup>11</sup> using blackness corrections of  $1.0 + 0.13D^2 + 0.17D^3$  and  $1.0 + 0.10D^2 + 0.10D^3$  respectively for Replica and Scientia plates. Smooth backgrounds were drawn on the levelled<sup>11</sup> form for the individual curves, modifying the curves to give the  $s/|f'_B(s)|/|f'_N(s)|$  type molecular intensities, and averaging the curves for each camera distance. The outer parts of the data

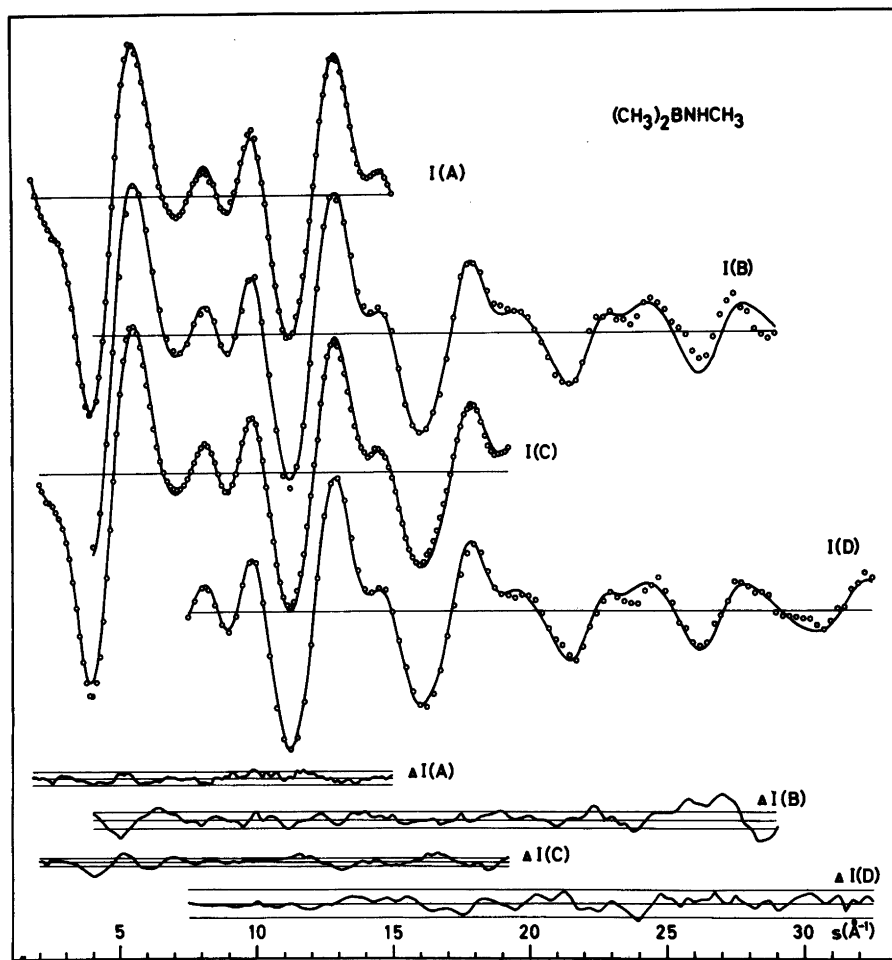


Fig. 1. Experimental modified molecular intensities (○) for  $(\text{CH}_3)_2\text{BNHCH}_3$  and the theoretical counterparts (full lines),  $I(\text{A})$ ,  $I(\text{B})$ ,  $I(\text{C})$  and  $I(\text{D})$ , respectively, for the 50, 25, 48 and 20 cm camera distances (see Table 1). The  $\Delta I$ -curves are the differences between the experimental and theoretical intensities, and the straight lines included are the estimated average uncertainties (three standard deviations) of the experimental intensity points.

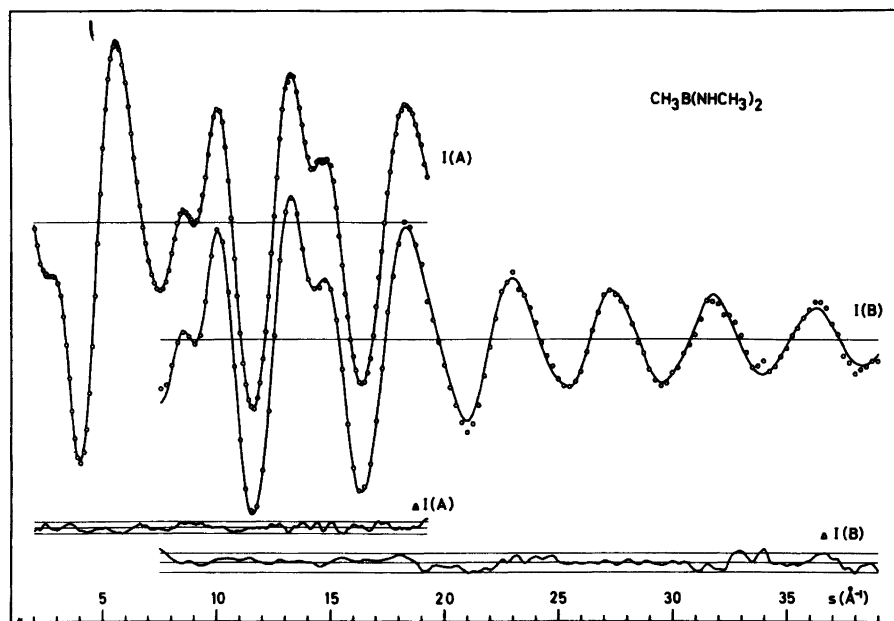


Fig. 2. Experimental modified molecular intensities (O) for  $\text{CH}_3\text{B}(\text{NHCH}_3)_2$  and the theoretical counterparts (full lines) presented as in Fig. 1.

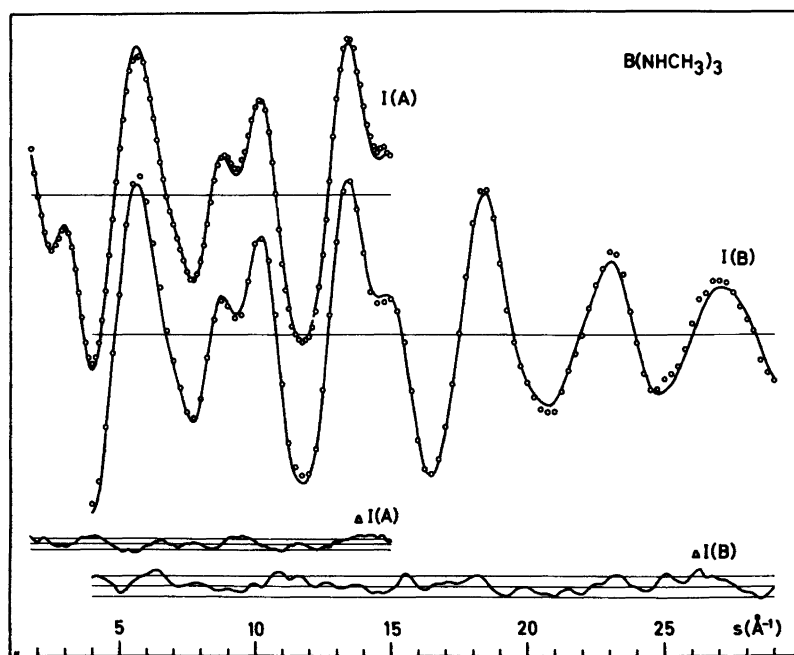


Fig. 3. Experimental modified molecular intensities (O) for  $\text{B}(\text{NHCH}_3)_3$  and the theoretical counterparts (full lines) presented as in Fig. 1.

from the Oslo-unit at the 20 cm camera distance, normally giving data to approximately  $43 \text{ \AA}^{-1}$  were discarded due to high noise to signal ratios determined in the averaging procedure. Inner parts of the data from the 25 cm camera distance of the Balzers Eldigraph were discarded due to high optical densities for which the applied blackness correction was uncertain. The scattering amplitudes and phases for the 35 and 42 keV electrons were calculated as described for the analogous methoxy boranes.<sup>2</sup>

## STRUCTURE ANALYSES

The structure determinations were carried out by the least-squares method, based on the intensity

data shown in Figs. 1–3. The employed diagonal weighting schemes are given in Table 1. The augmentative factor used for the standard deviations ( $\sigma = f\sigma_{LS}$ ) to account for data correlation, was estimated to  $f = 1.5$  from analyses of the BN2- and BN3 data as described previously.<sup>2</sup> Simplified general valence force field (SGVFF) for the molecules were derived, and computations of the vibrational amplitudes ( $l$ ), the shrinkage corrections ( $d$ ), the conversions from  $r_a$  to  $r_\alpha$  and to  $r_e$ , and the electron-diffraction anharmonicity coefficients ( $\kappa$ ) were carried out as described in Ref. 2 and references therein.

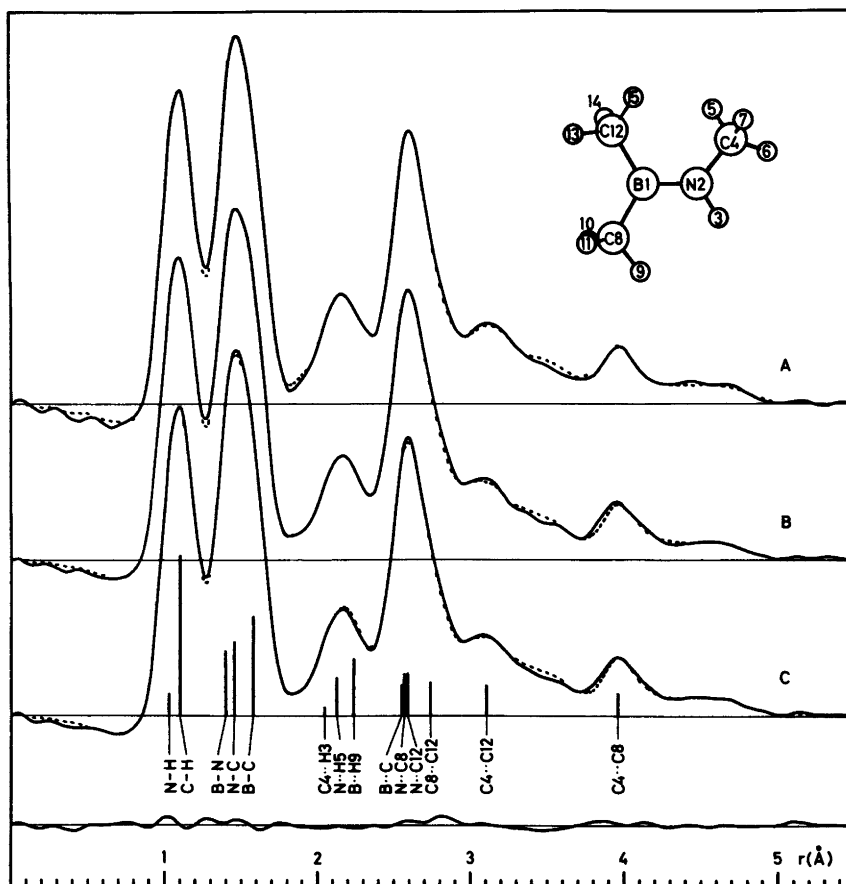


Fig. 4. Experimental (full lines) radial distribution curves for  $(\text{CH}_3)_2\text{BNHCH}_3$ : A, Balzers data; B, Oslo data; and C, all four data sets. The broken lines show the theoretical counterparts, and for the combined curve (C) the differences between experimental and theoretical values are also shown. The damping constant used was  $k = 0.0020 \text{ \AA}^2$ .

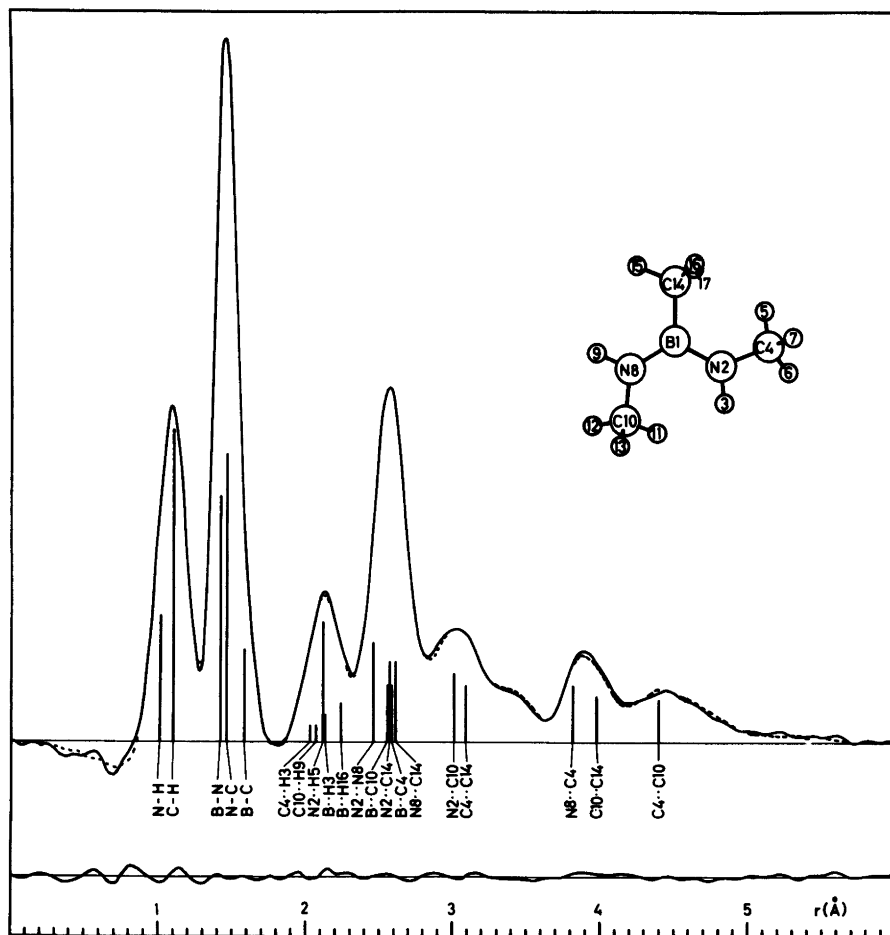


Fig. 5. Experimental (full line) and theoretical (broken line) radial distribution curves for  $\text{CH}_3\text{B}(\text{NHCH}_3)_2$ . The differences between experimental and theoretical values are also shown. The damping constant used was  $k=0.0012 \text{ \AA}^2$ .

### Geometrical models

The experimental *RD*-curves calculated using pertinent theoretical intensities for  $s < s(\text{min})$  in Table 1 are shown in Figs. 4–6. The inserted line diagrams show that the data are consistent with nearly coplanar heavy atom skeletons of the conformations shown by the models also given in Figs. 4–6.

The determinations of the B–N bond lengths were impeded by the overlapping N–C bond lengths (Figs. 4–6). Whereas their averages could be determined with high accuracy, the absolute values are highly interdependent and also strongly

correlated with the amplitudes of vibration associated with each bond. Therefore, the geometrical models of the molecules were described using the weighted average,  $\bar{r}$ , and the difference,  $\Delta$ , as variables. For BN2, symmetrically different B–N and N–C bonds and N–CH<sub>3</sub> groups were assumed to be equal, as were the B–C bonds and B–CH<sub>3</sub> groups in BN1. BN3 was assumed to possess C<sub>3</sub>-symmetry. Trivalent boron is known to be in coplanar arrangements with its three ligands, and also the amino-groups were assumed to be coplanar. The validity of assumed planarity of the B–N(H)C arrangements cannot be tested due to the

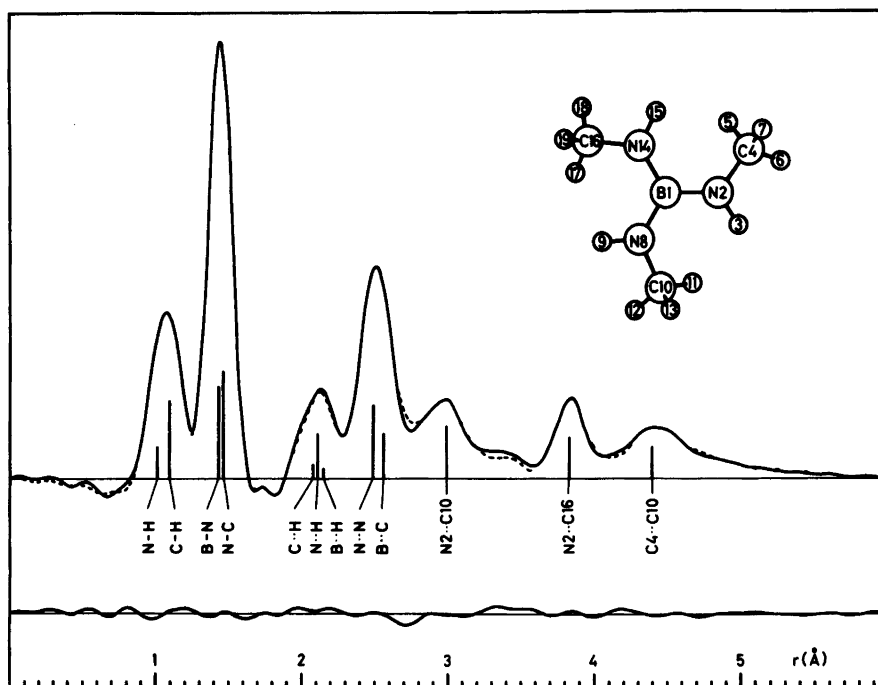


Fig. 6. Experimental (full line) and theoretical (broken line) radial distribution curves for  $B(NHCH_3)_3$ . The differences between experimental and theoretical values are also shown. The damping constant used was  $k = 0.0020 \text{ \AA}^2$ .

low contribution to the scattered intensity from the atom-pairs involving hydrogen. It is, however, consistent with results of earlier theoretical<sup>12</sup> and experimental<sup>13-16</sup> investigations. Local  $C_{3v}$ -symmetry was assumed for all methyl groups, and an average C-H bond had to be introduced (*i.e.*  $r(C_B-H) = r(C_N-H)$ ). The definitions of the geometrical variables are given subsequently with the final structural results (Tables 4-6).

#### Force field calculations

Vibrational spectral data of aminoboranes and related compounds have been reviewed elsewhere and some problems concerning unique assignments were discussed.<sup>17</sup> To our knowledge there are no reported vibrational spectral data for BN2, whereas such data are available for BN1<sup>18</sup> and BN3<sup>19-21</sup> for which, however, the lower frequency regions, *i.e.* below approximately  $300 \text{ cm}^{-1}$ , are lacking.

Force field calculations were carried out using atomic coordinates consistent with the bond distances and valence angles given in Tables 4-6, respectively for BN1, BN2 and BN3. However, models with symmetry planes through the heavy atoms were used, *i.e.*  $C_s$ -symmetry for BN1, a *syn,anti* form of  $C_s$ -symmetry for BN2, and  $C_{3h}$ -symmetry for BN3. The orientations of the methyl groups were in accordance with the preferences established by introductory refinements of such models, and correspond to all  $\theta(NC)$  angles as defined in Tables 4-6, equal to  $0^\circ$ .

An initial force field was designed for BN1 partly using force constants from SGVFF reported for  $B(CH_3)_3$ .<sup>2</sup> After adjustments so as to fit the calculated frequencies to experimental counterparts, the force constants for BN1 were used to obtain an initial force field for BN3. An SGVFF for BN2 was composed from the final force fields for BN1 and BN3, and the three sets of force constants are comprised in Table 2. The corresponding calculated vibrational fundamental frequencies with

Table 2. Simplified valence force fields for the series  $(\text{CH}_3)_2\text{BNHCH}_3$ ,  $\text{CH}_3\text{B}(\text{NHCH}_3)_2$  and  $\text{B}(\text{NHCH}_3)_3$ .

Definition <sup>a</sup>	BN1	BN2	BN3
$k_r$ (aJ $\text{\AA}^{-2}$ )			
B-C	3.60	3.60	—
B-N	6.00	5.70	5.20
N-C	5.00	5.00	4.70
N-H	6.61	6.61	6.61
C(B)-H	4.60	4.60	—
C(N)-H	4.80	4.80	4.80
$k_\theta$ (aJ $\text{rad}^{-2}$ )			
CBC	0.60	—	—
NBC	0.60	0.60	—
NBN	—	1.20	1.20
BNC	0.90	0.90	0.90
CNH	1.02	1.02	1.05
BCH	0.62	0.62	—
HC(B)H	0.45	0.45	—
NCH	0.87	0.87	0.87
HC(N)H	0.50	0.50	0.50
$k_t$ (aJ $\text{rad}^{-2}$ )			
BN	0.20	0.20	0.20
CB	0.03	0.03	—
CN	0.09	0.09	0.09
$k_\gamma$ (aJ $\text{rad}^{-2}$ )			
B	0.40	0.40	0.35
N	0.20	0.20	0.20
$k_{rr}$ (aJ $\text{\AA}^{-2}$ )			
BC/BC	0.40	—	—
BN/BC	0.40	0.40	—
BN/BN	—	0.40	0.40
BN/NC	—	—	0.85
$k_{r\theta}$ (aJ $\text{\AA}^{-1} \text{rad}^{-1}$ )			
NC/NCH	0.35	0.35	0.35
NC/CNH	0.30	0.30	0.30
BN/CNH	-0.25	-0.25	-0.30

<sup>a</sup> The meaning of the  $k$ -subscripts are:  $r$ , stretch;  $\theta$ , bend;  $\tau$  torsion; and  $\gamma$ , out-of-plane bend of a central atom in a planar four atom group. See molecular models in Figs. 4-6.  $1 \text{ aJ} = 10^{-18} \text{ J} = 1 \text{ mdyne } \text{\AA}$ .

approximate assignments are given in Table 3 which includes observed counterparts for BN1 and BN3.

The various methyl deformation ( $\delta$ ) and rocking ( $\rho$ ) modes are not identified in detail in the experimental material. As discussed for the series  $(\text{CH}_3)_3\text{B}$  to  $\text{B}(\text{OCH}_3)_3$ ,<sup>2</sup> reproductions of the relative magnitudes of in-plane and out-of-plane vibrations within each type (*i.e.*  $\delta(\text{BCH}_3)$ ,  $\delta(\text{NCH}_3)$ ,  $\rho(\text{BCH}_3)$  and  $\rho(\text{NCH}_3)$ ) are considered unimportant for the approximate force fields needed for our purpose.

For BN1 the  $\delta(\text{BCH}_3)$  vibration at  $1443 \text{ cm}^{-1}$  contains large contributions from B-C stretch, which is similar to what was encountered for  $(\text{CH}_3)_2\text{BOCH}_3$ .<sup>2</sup> However, the potential energy distribution (PED) identifies clearly  $\nu(\text{BC})$  to  $692 \text{ cm}^{-1}$ . The PED for the frequencies  $1172$  and  $1509 \text{ cm}^{-1}$  show that they are quite uncharacterized although they could be assigned to  $\nu(\text{BC})$  and  $\nu(\text{BN})$ , respectively. The in-plane CNH deformation at  $1346 \text{ cm}^{-1}$  was obtained by comparisons with BN3 for which the  $\delta(\text{CNH})$  modes were assigned to  $1388$  and  $1454 \text{ cm}^{-1}$  as compared to, for example,  $1320$  and  $1266 \text{ cm}^{-1}$  reported for *sym*-dimethylurea.<sup>22</sup>

For BN2 the calculated band at  $702 \text{ cm}^{-1}$  contained approximately equal contributions from  $\nu(\text{BC})$  and  $\nu(\text{BN})$ . According to the PED there are no other candidates for  $\nu(\text{BC})$  which consequently was assigned to  $702 \text{ cm}^{-1}$ . This left a rather uncharacterized frequency at  $1307 \text{ cm}^{-1}$  to be associated with  $\nu(\text{BN})$ . The higher  $\nu(\text{BN})$  frequency assigned to  $1509 \text{ cm}^{-1}$  was heavily mixed with  $\delta(\text{NCH}_3)$  modes and *vice versa* ( $\delta(\text{NCH}_3)$  at  $1531 \text{ cm}^{-1}$ ). The chosen assignments seem reasonable as compared to reported  $\nu(\text{BC})$  and  $\nu(\text{BN})$  frequencies at  $692$ ,  $1375$  and  $1510 \text{ cm}^{-1}$  for  $\text{CH}_3\text{B}(\text{N}(\text{CH}_3)_2)_2$ ,<sup>23</sup> and  $\nu(\text{BN})$  values of  $1307$  and  $1511 \text{ cm}^{-1}$  for  $\text{PhB}(\text{NHCH}_3)_2$ .<sup>24</sup> Difficulties in distinguishing between skeletal NBN and BNC deformations were encountered in BN2 as well as in BN3. The problems

Table 3. Fundamental vibrational frequencies ( $\text{cm}^{-1}$ ) for the series  $\text{CH}_3\text{BNHCH}_3$ ,  $\text{CH}_3\text{B}(\text{NHCH}_3)_2$  and  $\text{B}(\text{NHCH}_3)_3$  as calculated from the force fields in Table 2. Observed values are listed for BN1 and BN3.

Approximate assignments <sup>a</sup>	BN1		BN2	BN3		Reass. <sup>b</sup>
	Calc.	Obs. Ref. 18	Calc.	Calc.	Obs. Ref. 20, 21	
$\nu(\text{NH})$	—	—	3461	3461	3420	3465
$\nu(\text{BC})$	3461	3458	3462	3462E		3445E
	692 <sup>b</sup>	682	702 <sup>b</sup>	—	—	—
	1172 <sup>b</sup>	1176	—	—	—	—



Table 3. Continued.

$\nu(\text{BN})$	'	—	—	1307	729	—	724	
	'	1509	1515	1507	1468E	1499	1474E	
$\nu(\text{NC})$	'	1055	1060	1039	1037E		1021E	
	'	—	—	1130	1042	1027	1038	
$\delta(\text{CNH})$	'	1346 <sup>b</sup>	?	1380	1379E		1388	
	'	—	—	1439	1403		1454	(1426?)
$\delta(\text{CBC})$	'	306	316	—	—		—	
$\delta(\text{NBC})$	'	197	?	229	—		—	
$\delta(\text{NBN})$	'	—	—	498 <sup>b</sup>	512E <sup>b</sup>		624E	Dp?
$\delta(\text{BNC})$	'	—	—	173 <sup>b</sup>	174E <sup>b</sup>		310E(229)	unobs.?
	'	436	407	389	305		320	
$\gamma\text{N}$	"	773	760	795	813	704	1274	800(703)
	"	—	—	766	753E	714	1106E	787(714)
$\gamma\text{B}$	"	475	477	509	522		500	
$\tau(\text{BN})$	"	160	?	182	122		(107)	
	"	—	—	156	162E		(156)	
Methyl								
$\nu(\text{C}_\text{B}\text{H})$	'	2838		—	—		—	
	'	2839		—	—		—	
	'	2935		2835	—		—	
	'	2936		2937	—		—	
	"	2935	2830	2937	—		—	
	"	2935	2896	—	—		—	
$\nu(\text{C}_\text{N}\text{H})$	'	—	2945	2895	2892		2846	
	'	—	3005	2896	2892E		2885E	
	'	2890		3002	3005	2865	2925E	
	'	3006		3004	3005E	2911	2990	
	"	3004		3001	3003		2807	
	"			3004	3003E		2894E	
$\delta(\text{BCH}_3)$	'	1287		—	—		—	
	'	1301		—	—		—	
	'	1428		1319	—		—	
	"	1443 <sup>b</sup>	1285	1478	—		—	
	"	1287 <sup>b</sup>	1323	1326	—		—	
	"	1301	1434	—	—		—	
$\delta(\text{NCH}_3)$	'	—	1444	1415	1427E		1434	?
	'	—	1504	1420	1446		1425	(1454)
	'	1416		1522	1523	1386	?	1488E
	'	1485		1531	1534E	1435	?	1497E
	"	1427		1427	1444			1434
	"	—		1428	1444E			1540E''
$\rho(\text{BCH}_3)$	'	885		—	—		—	
	'	898		911	—		—	
	"	920		994	—		—	
	"	1017	868	—	—		—	
$\rho(\text{NCH}_3)$	'	—	936	1071	1114E		—	1116
	'	1095	949	1112	1119	1139	—	1147E
	"	1142		1134	1148E	1189	1184, 1147	1106
	"	—		1138	1152	1277	1246, 1135E	1274E
$\tau(\text{BCH}_3)$	"	124	?	—	—		—	
	"	128	?	125	—		—	
$\tau(\text{NCH}_3)$	"	215	?	208	200		?	
	"	—	—	233	239E		?	

<sup>a</sup> Vibrations symmetric and asymmetric with respect to the skeleton ( $C_3$ -symmetry) are identified by ' and "", respectively. The degenerate modes for  $\text{B}(\text{NHCH}_3)_3$  ( $C_{3h}$ -symmetry) are identified by E after the calculated value. <sup>b</sup> See text for comments on reassignments, mixed modes and uncertain assignments. <sup>c</sup> Parenthesized values are calculated from force fields in Ref. 19.

Table 4. Results for  $(\text{CH}_3)_2\text{BNHCH}_3$ , distance ( $r$ ) and amplitude ( $l$ ) quantities in Å and angles ( $\angle, \theta$ ) in degrees. The numbering of the atoms is given in Fig. 4.

	SGVFF <sup>a</sup>		ED (Oslo) <sup>b</sup>		ED (Balzers) <sup>b</sup>		ED (Combined) <sup>b</sup>	
	$10^4\Delta r$	$l_{\text{calc}}$	$l_{\text{ED}}$	$r_{\text{a}}, \angle, \theta$	$l_{\text{ED}}$	$r_{\text{a}}, \angle, \theta$	$l_{\text{ED}}$	$r_{\text{a}}, \angle, \theta$
N-H	(187)	0.0728	0.0728 <sup>c</sup>	1.016(9)	0.0728 <sup>c</sup>	1.045(16)	0.0728 <sup>c</sup>	1.026(8)
C <sub>B</sub> -H	(708)	0.0791	0.0785 <sup>c</sup>	1.109(2)	0.0785 <sup>c</sup>	1.107(3)	0.0785 <sup>c</sup>	1.105(3)
C <sub>N</sub> -H	(350)	0.0782						
B-C	(34)	0.0530	0.053 <sup>c</sup>	1.587(2)	0.053 <sup>c</sup>	1.582(2)	0.053 <sup>c</sup>	1.586(2)
$\bar{r}(\text{NC}, \text{BN})$	—	—	—	1.426(2)	—	1.427(2)	—	1.427(2)
$\Delta(\text{NC}, \text{BN})$	—	—	—	0.064(3)	—	0.054(4)	—	0.060(3)
B-N	(26)	0.0458	0.0458 <sup>c</sup>	1.394(2)	0.0458 <sup>c</sup>	1.400(3)	0.0458 <sup>c</sup>	1.397(2)
N-C	(96)	0.0483	0.0483 <sup>c</sup>	1.458(2)	0.0483 <sup>c</sup>	1.454(2)	0.0483 <sup>c</sup>	1.456(2)
N...H5	—	0.103	0.103	2.123(9)	0.103	2.133(12)	0.103	2.127(8)
B...H9	—	0.112	0.112	2.250(9)	0.112	2.237(10)	0.112	2.243(7)
C4...H3	—	0.098	0.098 <sup>c</sup>	2.048(11)	0.098 <sup>c</sup>	2.042(16)	0.098 <sup>c</sup>	2.048(10)
B...H3	—	0.103	0.103	2.115(8)	0.103	2.146(15)	0.103	2.126(8)
N...C8	28	0.074	0.077	2.586(11)	0.074	2.582(16)	0.076	2.574(7)
N...C12	37	0.073	0.076	2.581(11)	0.073	2.576(20)	0.075	2.591(7)
C8...C12	42	0.079	0.080 <sup>(2)</sup>	2.737(7)	0.079 <sup>(3)</sup>	2.741(9)	0.081 <sup>(2)</sup>	2.738(6)
B...C4	72	0.070	0.071	2.551(8)	0.070	2.575(10)	0.072	2.557(7)
C4...C12	96	0.132	0.132(10)	3.092(10)	0.122(11)	3.126(11)	0.129(7)	3.109(9)
C4...C8	141	0.077	0.079(6)	3.960(9)	0.079(9)	3.962(8)	0.078(5)	3.961(7)
$\angle \text{BNH}$				122.0 <sup>c</sup>		122.0 <sup>c</sup>		122.0 <sup>c</sup>
$\angle \text{BCH}$				112.0(7)		111.4(8)		111.5(5)
$\angle \text{NCH}$				110.9(7)		112.1(9)		111.3(6)
$\theta(\text{H9C8BN2})$				0.°		0.°		0.°
$\theta(\text{H13C12BC8})$				30.°		30.°		30.°
$\theta(\text{H5C4N2B})$				-30.°		-30.°		-30.°
$\angle \text{BNC4}$				127.5(7)		129.5(10)		128.0(6)
$\angle \text{NBC8}$				120.4(9)		120.0(13)		119.4(5)
$\angle \text{NBC12}$				120.1(8)		119.6(14)		120.8(5)
$\theta(\text{C4N2BC12})$				14.4(63)		-15.4(86)		7.9(62)
$R_w(\%)$				7.25		6.87		7.44

<sup>a</sup>The force field is given in Table 2. The parenthesized  $\Delta r$  values are the calculated  $r_{\text{a}} - r_{\text{e}}$  values, and  $\Delta r$  for the nonbond distances is the shrinkage ( $d$ ) of that distance. <sup>b</sup>The distance and angle parameters within braces correspond to the independent geometrical parameters described in the text. <sup>c</sup>Parameters maintained at constant values during the refinement. See text.

are similar to those described for the oxygen analogues.<sup>2</sup>

The most extensive set of vibrational spectral data for  $\text{BN}_3$ <sup>19</sup> appears in our opinion to contain some surprising assignments, in particular for the methyl modes,  $\delta(\text{CH}_3)$  and  $\rho(\text{CH}_3)$ , and for the out-of-plane NH bending,  $\gamma(\text{N})$ . See Table 3. Firstly, there are no assignments of out-of-plane methyl deformations in the 1400–1500  $\text{cm}^{-1}$  region nor in-plane modes for the 1100–1240  $\text{cm}^{-1}$  region, whereas four out-of-plane fundamentals have been given for the latter range. Secondly, according to the reported PED<sup>19</sup> the  $\gamma(\text{N})$  frequencies are assigned to rather high

values as compared to previous assignments for  $\text{BN}_3$ ,<sup>20</sup> which seem consistent with the  $\gamma(\text{N})$  modes reported for  $(\text{CH}_3)_2\text{BNH}_2$  and  $(\text{CH}_3)_2\text{BNHCH}_3$ .<sup>18</sup> Predictions for the amide NH out-of-plane modes to the 400–800  $\text{cm}^{-1}$  region and the assigned values of 672 and 720  $\text{cm}^{-1}$  reported for *sym*-dimethylurea,<sup>22</sup> seem to support the old assignment. Therefore, we would prefer an assignment of the 1274  $\text{cm}^{-1}$  frequency to  $\rho(\text{CH}_3)$  as in the earlier study,<sup>20</sup> although it might appear somewhat high. It is interesting to note that the spectral data also given for  $\text{B}(\text{NDCH}_3)_3$ ,<sup>19</sup> contain medium strong Raman and IR bands at,

Table 5. Results for  $\text{CH}_3\text{B}(\text{NHCH}_3)_2$ , distance ( $r$ ) and amplitude ( $l$ ) quantities in Å and angles ( $\angle, \theta$ ) in degrees. The numbering of the atoms is given in Fig. 5.

	SGVFF <sup>a</sup>		ED( $R_w = 4.45\%$ ) <sup>b</sup>			
	$10^4 \Delta r$	$l_{\text{calc}}$	$l_{\text{ED}}$	$r_a$	Angles	
N-H	(195)	0.0728	0.073 <sup>c</sup>	1.008(4)	$\angle$ BNH	122.° <sup>c</sup>
C <sub>B</sub> -H	(744)	0.0791	0.078	1.102(2)	$\angle$ BCH	111.4(12)
C <sub>N</sub> -H	(357)	0.0782			$\angle$ NCH	
B-C	(44)	0.0527	0.0527	1.586(3) <sup>b</sup>	$\theta$ (H15C14BN8)	0.° <sup>c</sup>
$\bar{r}(\text{NC, BN})$	—	—	—	1.437(2)	$\theta$ (H5C4N2B)	18.2(42)
$\Delta(\text{NC, BN})$	—	—	—	0.038(3)	$\theta$ (H11C10N8B)	
B-N	(32)	0.0463	0.046 <sup>c</sup>	1.418(2)	$\angle$ NBN	120.4(3)
N-C	(88)	0.0482	0.048 <sup>c</sup>	1.456(2)	$\angle$ N3BC14	118.0(10)
N2...H5	—	0.102	0.097	2.122(4)	$\angle$ BN2C4	128.4(9)
B...H16	—	0.112	0.107	2.237(4)	$\angle$ BN8C10	126.4(5)
C4...H3	—	0.098	0.093	2.030(11)	$\theta$ (C4N2BC14)	16.9(23)
C10...H9	—	0.098	0.093	2.073(7)	$\theta$ (C10N8BN2)	
B...H3	—	0.103	0.098	2.131(4)		
N2...N8	21	0.062	0.065	2.459(4)		
B...C4	69	0.070	0.073	2.581(10)		
B...C10	60	0.071	0.074	2.560(6)		
N2...C14	39	0.072	0.075	2.572(14)		
N8...C14	32	0.072	0.075	2.620(12)		
N2...C10	81	0.116	0.113	3.013(14)		
C4...C14	103	0.127	0.124	3.089(14)		
N8...C4	111	0.070	0.072	3.824(7)		
C10...C14	130	0.076	0.078	3.977(9)		
C4...C10	103	0.126	0.126	4.394(14)		

<sup>a-c</sup> See footnotes of Table 4.

Table 6. Results for  $\text{B}(\text{NHCH}_3)_3$ , distances ( $r$ ) and amplitude ( $l$ ) quantities in Å and angles ( $\angle, \theta$ ) in degrees. The numbering of the atoms is given in Fig. 6.

	SGVFF <sup>a</sup>		ED( $R_w = 6.92\%$ ) <sup>b</sup>			
	$10^4 \Delta r$	$l_{\text{calc}}$	$l_{\text{ED}}$	$r_a$	Angles	
N-H	(220)	0.072	0.072 <sup>c</sup>	1.022(8)	$\angle$ BNH	122.° <sup>c</sup>
C-H	(413)	0.078	0.078 <sup>c</sup>	1.094(4)	$\angle$ NCH	111.1(6)
$\bar{r}(\text{NC, BN})$	—	—	—	1.446(2) <sup>b</sup>	$\theta$ (H5C4N2B)	24.7(35) <sup>b</sup>
$\Delta(\text{NC, BN})$	—	—	—	0.026(4)	$\angle$ BNC	125.2(4)
B-N	(36)	0.0481	0.0481 <sup>c</sup>	1.432(2)	$\theta$ (C4N2BN14)	13.3(21)
N-C	(130)	0.0500	0.0500 <sup>c</sup>	1.459(3)		
N2...H5	—	0.102	0.099	2.115(7)		
C4...H3	—	0.098	0.095	2.080(7)		
B...H3	—	0.104	0.101	2.155(7)		
N...N	25	0.063	0.072	2.478(4)		
B...C4	81	0.072	0.081	2.558(5)		
N2...C10	100	0.119	0.125(7)	2.993(7)		
N2...C16	149	0.071	0.086(6)	3.829(5)		
C4...C10	251	0.126	0.131(10)	4.395(13)		

<sup>a-c</sup> See footnotes of Table 4.

respectively, 1278 and 1122  $\text{cm}^{-1}$ , which were left unassigned.<sup>19</sup> An attempt to reassign the  $\delta(\text{CH}_3)$  and  $\rho(\text{CH}_3)$  frequencies is presented in Table 3, and there appear to be two possibilities for assignments of  $\gamma(\text{N})$  to weak bands in the 700–800  $\text{cm}^{-1}$  region.

The reported force fields give calculated fundamental frequencies in only a rough agreement with the available vibrational spectral data. However, it was not found worthwhile to pursue the fitting procedure. It is interesting to note that the  $k_r(\text{BN})$  values (Table 2) happen to indicate a small weakening of the BN bond throughout the series BN1 to BN3. This fact should, however, not be stressed due to the large uncertainties of the derived force constants, and also potential failure of the force constants to reflect pure B–N stretch as is often encountered in molecules with many atoms of similar masses.

### Structure refinements

The structural refinements were carried out essentially for two models: firstly, coplanar heavy atom skeletons were imposed on the molecules, and secondly, these constraints were relaxed by refining the various  $\theta(\text{BN})$  parameters. As described for the oxygen analogues,<sup>2</sup> shrinkage corrections ( $d$ ) were carried out only for the skeletal nonbonded distances, and it was found that the  $l$ - and  $d$ -values calculated for planar models could be used even for  $\theta(\text{BN})$  parameters of 10–15°. The skeletal shrinkages, the  $r_s$  to  $r_a$  corrections for bond distances and the more important  $l$ -values calculated from the force fields in Table 2 are given in Tables 4–6. Generally  $l$ -values associated with distances involving hydrogens not shown in the

tables were fixed at the calculated values. The calculated values were also used for other distances and in grouped refinements of amplitudes by maintaining the calculated differences within each group. Both types of models were refined for all  $l$ -values fixed and for as many amplitude parameters as possible included in the refinement procedure.

The conformational orientations of the methyl groups could not be refined for BN1 and BN2, and the constraints or fixed values used in the final refinements were in accordance with results from systematic searches for sets of values which gave best agreement with the data. The  $l$ -values used in the final refinements were calculated using atomic coordinates consistent with the given  $\theta(\text{NC})$  values in Tables 4–6.

For all molecules  $\angle \text{BNH}$  represented a problem in the sense that it invariably refined to large values with large standard deviations. It was concluded that this parameter could not be determined and it was fixed at 122° for all molecules.

In the oxygen counterparts of BN1 and BN2 substantial deviations from ideal trigonal ( $\angle = 120^\circ$ ) arrangements around the borons were established. However, for BN1 and BN2 the valence angles invariably refined to values close to 120°, also from start values consistent with those of the oxygen analogues.

The parameter values for the three molecules given in Tables 4–6 and in Fig. 7, are chosen to represent the final results. Comparisons of calculated and experimental counterparts are shown, respectively, for BN1, BN2 and BN3 in Figs. 1–3 for the intensities, and Figs. 4–6 for the radial distributions. Also, the least-squares agreement factors,<sup>11</sup>  $R_w = \sum w(s)\Delta^2(s)/\sum w(s)I_{\text{obs}}^2(s)$ , given in

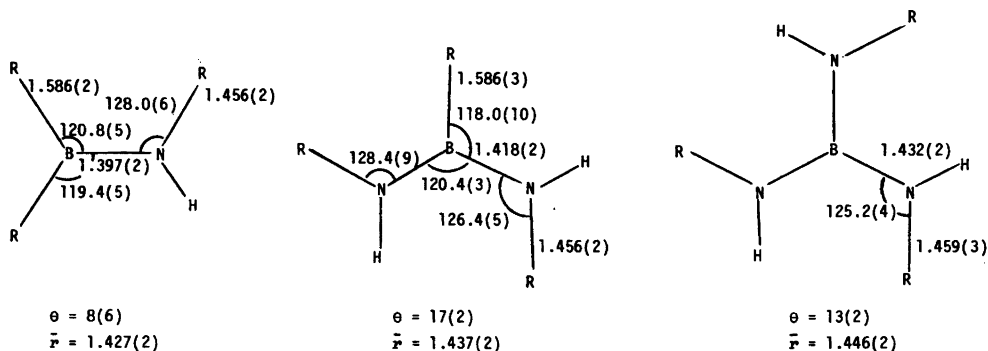


Fig. 7. Nonhydrogen structural results for  $\text{R}_2\text{BNHR}$ ,  $\text{RB(NHR)}_2$  and  $\text{B(NHR)}_3$  were  $\text{R} = \text{CH}_3$ . Distances in Å and angles in degrees. (cf. Tables 4–6).

Table 7. Standard deviations ( $\sigma_{Ls}$ ,  $r$  and  $l$  in Å;  $\angle$  and  $\theta$  in degrees) and the elements of the correlation matrices,  $|\rho_{ij}| \geq 50\%$ , for the structural results in Tables 4–6. The  $K1$  to  $K4$  values are the scale constants.

BN1	$\sigma_{Ls}$	i j, $\rho_{ij}$	BN2	$\sigma_{Ls}$	i j, $\rho_{ij}$	BN3	$\sigma_{Ls}$	i j, $\rho_{ij}$
$\bar{r}(\text{NC, BN})$	0.0005	1	$\bar{r}(\text{NC, BN})$	0.0003	1	$\bar{r}(\text{NC, BN})$	0.0005	1
$\Delta(\text{NC, BN})$	0.0016	2	$\Delta(\text{NC, BN})$	0.0017	2	$\Delta(\text{NC, BN})$	0.0027	2
$r(\text{NH})$	0.0055	3	$r(\text{NH})$	0.0027	3	$r(\text{NH})$	0.0054	3
$r(\text{CH})$	0.0008	4 3, -64	$r(\text{CH})$	0.0008	4	$r(\text{CH})$	0.0025	4 3, -65
$\angle \text{BNC4}$	0.39	5	$\angle \text{BN2C4}$	0.61	5	$\angle \text{BNC}$	0.24	5
$\angle \text{NCH}$	0.38	6	$\angle \text{BCH} = \angle \text{NCH}$	0.19	6	$\angle \text{NCH}$	0.39	6
$\theta(\text{NB})$	4.17	7	$\theta(\text{CN})$	2.76	7	$\theta(\text{CN})$	2.32	7
$\angle \text{NBC8}$	0.35	8 7, +74	$\theta(\text{BN})$	1.50	8	$\theta(\text{BN})$	1.42	8
$r(\text{BC})$	0.0007	9	$\angle \text{NBN}$	0.17	9	$\theta(\text{BN})$	1.42	8
$\angle \text{BCH}$	0.35	10 6, -50	$\angle \text{BN8C10}$	0.35	10	$l(\text{N2}\cdots\text{H5})$	0.0026	9
$\angle \text{NBC12}$	0.31	11 7, -50; 8, -76	$\angle \text{N2BC14}$	0.66	11	$l(\text{N}\cdots\text{N})$	0.0019	10 5, -50
$l(\text{N}\cdots\text{C8})$	0.0011	12	$r(\text{BC})$	0.0018	12	$l(\text{N2}\cdots\text{C10})$	0.0047	11 7, +50
$l(\text{C4}\cdots\text{C12})$	0.0048	13	$l(\text{N2}\cdots\text{H5})$	0.0016	13	$l(\text{N2}\cdots\text{C16})$	0.0037	12
$l(\text{C4}\cdots\text{C8})$	0.0035	14	$l(\text{N2}\cdots\text{N8})$	0.0021	14	$l(\text{C4}\cdots\text{C10})$	0.0069	13
$K1 = 45.9$	0.32	15	$l(\text{N2}\cdots\text{C10})$	0.0039	15	$K1 = 44.8$	0.32	14
$K2 = 44.5$	0.33	16	$l(\text{N8}\cdots\text{C4})$	0.0046	16	$K2 = 45.7$	0.40	15
$K3 = 46.8$	0.46	17	$l(\text{C4}\cdots\text{C14})$	0.0079	17			
$K4 = 44.2$	0.58	18	$K1 = 45.3$	0.24	18			
			$K2 = 43.0$	0.36	19			
					2, +58; 12, +61			
					2, +67; 18, +54			

Tables 4–6 reflect the goodness of the least-squares fits. The estimated standard deviations including effects from data correlation and for the distances, the uncertainty in the  $s$ -scale, are given in parentheses. The least-squares standard deviations actually obtained in the refinements ( $\sigma_{LS}$ ) are given in Table 7 together with elements from the correlation matrices.

As for the analogous oxygen compounds,<sup>2</sup> the final results are obtained using calculated values for the amplitudes associated with the skeletal bonds. Refinements of this amplitude group gave inconsistent changes relative to the calculated values for the various data sets and molecules. These shifts were accompanied with changes in the  $\Delta$ -parameters whereas  $\bar{r}$  and for BN2 and BN1 also  $r(\text{BC})$  remained unaffected. For BN3, BN2 and the Oslo and Balzers data sets for BN1, respectively the  $l$ -value group, represented here by  $l(\text{BN})$ , refined to 0.043(2), 0.045(1), 0.052(2) and 0.057(3) Å, and the corresponding  $\Delta$  parameters were 0.031(5), 0.040(3), 0.058(4) and 0.040(7) Å. As compared to the pertinent results given in Tables 4–6 this resulted in substantial changes in  $r(\text{BN})$ , and it demonstrates the correlation of the determination of  $r(\text{BN})$  with the assumptions introduced for the bond-distance amplitudes. Therefore, any change in the B–N bond throughout the series of molecules should be considered in relation to any such variation in the averages of  $r(\text{BN})$  and  $r(\text{NC})$ , *i.e.*  $\bar{r}$ , which are not affected by the uncertainties in these amplitudes.

As seen from Tables 4–6 the heavy atom skeletons are found to be slightly nonplanar as reflected by the various  $\theta(\text{BN})$  parameters given. For BN2, the torsional angles of the *syn,anti* form were at first refined independently, but significant differences were not obtained when the torsions of the two aminogroups were set equal, *i.e.* the dihedral angles are equal as defined by, respectively, the C–N–B–C and C–N–B–N arrangements. Indications of coexisting second conformers, like the *syn,syn* or *anti,anti* periplanar forms, were not observed. The significance of the deviations from planarity may also be judged by conferring to the  $R_w$ -factors obtained when planar heavy atom skeletons were imposed on the molecules: BN3, 6.92%; BN2, 4.63%; BN1 (Oslo data), 7.28%; and BN1 (Balzers data) 6.92%.

Comparisons of the structural results for BN1 obtained from the two different data sets (Table 4) reveal that the Balzers data yield  $\Delta$ -values consistently lower than the Oslo data, for all

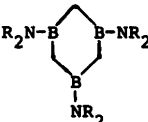
$R_2\text{B-NHR}$	$r_a = 1.397(2)$	ED
	$(r_e = 1.392)$	
$\text{H}_2\text{B-NH}_2$	$r_e = 1.398$	MO <sup>5</sup>
	$r_s = 1.391(2)$	MW <sup>25</sup>
$R_2\text{B-NR}_2$	$\bar{r} = 1.42(3)$	XR <sup>14</sup>
	$\bar{r} = 1.400$	XR <sup>16</sup>

Fig. 8. The B–N bond distance (in Å) obtained in the present study of BN1 compared with  $r(\text{BN})$ -values in some related compounds as obtained in molecular orbital calculations (MO), by microwave (MW) and electron-diffraction (ED) studies of gases and by X-ray-diffraction (XR) studies of crystals.  $R = \text{CH}_3$ .

reasonable assumptions imposed on the models and amplitudes and for various changes in the data ranges used in the refinements. Also, the torsional angles are of opposite sign, but neither is significantly different from zero. Other comparisons suggest that serious scale inconsistencies for the two experiments are not present. After confirming a presumed nonimportant difference in the scattering functions for 35 and 42 keV electrons, combined refinements were carried out based on the altogether four intensity curves, and the results (Table 4) are chosen to represent our final structure for BN1.

## DISCUSSION

The structural results concerning the non-hydrogen atoms of BN1 to BN3 are shown in Fig. 7. Figs. 8–10 comprise some B–N bond length comparisons for molecules containing respectively B–N, B(–N)<sub>2</sub> and B(–N)<sub>3</sub> type of bonding where the other ligands to boron are hydrogens or carbons.

The determinations of  $\theta(\text{BN})$  to 8(6), 17(2) and 13(2)°, respectively, for BN1, BN2 and BN3, suggest that deviation from planarity is not significant for BN1, whereas small deviations are indicated for BN2 and BN3. It should be noted that for  $(\text{CH}_3)_2\text{BOCH}_3$ ,<sup>2</sup> a nonplanar model with  $\theta(\text{BO}) = 14(4)^\circ$  could preferably be substituted by a dynamic model with 11° for the root-mean-square torsional amplitude ( $\delta$ ) about  $\theta(\text{BO}) = 0^\circ$ . This


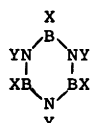
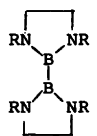
$\text{RB}(\text{NHR})_2$	$r_a = 1.418(2)$ ( $r_e = 1.413$ )	ED
$\text{HB}(\text{NH}_2)_2$	$r_e = 1.424$ $r_s = 1.418$	MO <sup>5</sup> MW <sup>26</sup>
$\text{HB}(\text{NR}_2)_2$	$r_a = 1.42$	ED <sup>27</sup>
$\text{RB}(\text{NR}_2)_2$	$r_a = 1.44$	ED <sup>27</sup>
	$r_a = 1.413 \pm 0.010$	ED <sup>28</sup>
	X=Y=H: $r_a = 1.436 \pm 0.002$ X=H, Y=R: $r_a = 1.42(2)$ X=Y=Et: $r = 1.423 \pm 0.015$ X=Y=Ph: $r = 1.441$	ED <sup>29</sup> ED <sup>30</sup> XR <sup>31</sup> XR <sup>32</sup>
	$\bar{r} = 1.413 \pm 0.012$	XR <sup>33</sup>

Fig. 9. The B–N bond distance (in Å) obtained for BN2 compared with  $r(\text{BN})$  in related compounds. R = CH<sub>3</sub>, Et = C<sub>2</sub>H<sub>5</sub> and Ph = C<sub>6</sub>H<sub>5</sub>.

corresponds fairly well to the  $\delta$ -estimate based on the torsional force constant, and the estimated  $k_t(\text{BN})$ -values would suggest  $\delta$ -values of about 8°. Thus,  $\theta(\text{BN})$  values different from zero may partly be ascribed to large amplitude motion about the B–N bonds. It is, however, also likely that steric repulsions between neighbouring monomethylamino groups would cause out-of-plane distortions. In this connection it is interesting to note that the H3...H11 distances for BN2 and BN3 (see Figs. 5 and 6) approach 2.1 Å when skeletal planarity is imposed on the molecules, whereas these distances are respectively 2.34(6) and 2.29(6) Å in the nonplanar models. The permethylated tris(amino)borane<sup>34</sup> exhibits greater distortions from planarity with a  $\theta(\text{BN})$  value of 33(3)°. This is consistent with increased steric repulsion upon increased methylsubstitution and serves to justify the notion that the non-zero  $\theta(\text{BN})$  values of BN2 and BN3 probably reflect real distortions from planarity. The planar or near planar conformations of the molecular skeletons reflect the importance of  $\pi$ -bonding which is maximized in the planar forms. It has been stated<sup>39</sup> that the exocyclic B–N bond in

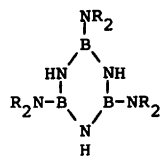
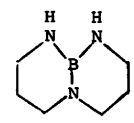
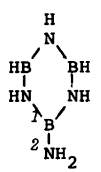
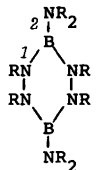
$\text{B}(\text{NHR})_3$	$r_a = 1.432(2)$ ( $r_e = 1.428$ )	ED
$\text{B}(\text{NH}_2)_3$	$r_e = 1.439$	MO <sup>5</sup>
$\text{B}(\text{NR}_2)_3$	$r_a = 1.431(12)$	ED <sup>34</sup>
$\text{B}(\text{HNHR}_2)_3$	$\bar{r} = 1.420(14)$	XR <sup>35</sup>
	$\bar{r} = 1.432$	XR <sup>15</sup>
	$\bar{r} = 1.421$	XR <sup>36</sup>
	1: $\bar{r}_a = 1.418 \pm 0.004$ 2: $r_a = 1.498 \pm 0.008$	ED <sup>37</sup>
	2: $\bar{r} = 1.429(4)$ 1: $\bar{r} = 1.433(4)$	XR <sup>38</sup>

Fig. 10. The B–N bond distance (in Å) obtained for BN3 compared with  $r(\text{BN})$  in related compounds. R = CH<sub>3</sub>.

hexakis(trimethylsilyl)-2,4-diamino-1,3,2,4-diazadiboretidin is surprisingly short (1.45 Å) as related to the fact that the substituents on the B and N atoms are arranged nearly perpendicularly to one another, thus not allowing for formation of a classical  $\pi$ -bond. It is also noteworthy that in *B*-monoaminoborazine (Fig. 10) where the amine group is claimed to be nonplanar, the exocyclic B–N bond is determined to be substantially longer than the average of the ring B–N bonds.<sup>37</sup> However, it appears that low precision in the determination of  $r(\text{BN})$  would make attempts to correlate corresponding  $r(\text{BN})$  and  $\theta(\text{BN})$  values rather futile for small changes in the torsional angle. For example, an increase in  $\theta(\text{BN})$  from 13(2)° in B(NHCH<sub>3</sub>)<sub>3</sub> to 33(3)° in B(N(CH<sub>3</sub>)<sub>2</sub>)<sub>3</sub>,<sup>34</sup> is not accompanied by significant B–N bond elongation as judged from the  $r(\text{BN})$

values given in Fig. 10.

Comparisons of ED-results for the BN1 to BN3 series with the available MO-<sup>5</sup> and MW-results<sup>25,26</sup> for H<sub>2</sub>BNH<sub>2</sub>, HB(NH<sub>2</sub>)<sub>2</sub> and B(NH<sub>2</sub>)<sub>3</sub> do not suggest significant differences in the B–N bonds in hydrogen and methyl counterparts (Figs. 8–10). These studies also seem to establish a significant and consistent B–N bond elongation throughout these two series of compounds. If the variation in the degree of  $\pi$ -character of the B–N bonds is dominating the bond length changes, these results are in consonance with the expected decrease in  $\pi$ -bonding as judged from the fact that the possibilities for  $\pi$ -electron backdonation to boron would be smaller as more donors compete for the one  $\pi$ -electron accepting orbital of boron. However, when also other compounds are considered (Figs. 8–10), variations in the B–N bond lengths within each group of compounds are noted, and this prevents a more general statement about correlation between the B–N bond length and the expected  $\pi$ -bond variations.

The B–N bond of 1.397(2) Å in BN1 is longer than the bonds of  $1.379 \pm 0.006$  and 1.380(6) Å found in the dichloroboranes, (CH<sub>3</sub>)<sub>2</sub>NBCl<sub>2</sub><sup>13</sup> and (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>NBCl<sub>2</sub>,<sup>40</sup> which to our knowledge are the shortest B–N bonds of this type observed.

The N–C bonds (Fig. 7) compare favourably with  $r(\text{NC}) = 1.454(2)$  Å found for trimethylamine<sup>41</sup> which is consistent with N–C bond lengths in various compounds with (methylamino)borane moieties, as determined in studies by gaseous electron diffraction,<sup>28,34,42,43</sup> and by crystallographic X-ray diffraction.<sup>15,16,35</sup> The B–C bonds in the present aminoboranes (Fig. 7) seem to be slightly longer than the  $r_a(\text{BC})$  value of 1.577(1) Å for B(CH<sub>3</sub>)<sub>3</sub>.<sup>44</sup> The  $r(\text{BC})$  values determined for other boraneamines<sup>27</sup> seem to corroborate this trend, which appears opposite to that noted for various thio- and oxy-boranes.<sup>2</sup>

*Acknowledgements.* Mrs. S. Gundersen and Mr. H. V. Volden are gratefully acknowledged for densitometering the photographic plates and for figure preparations. We also want to express our gratitude to Professor H. Nöth for providing the samples and for stimulating discussions, and to Dr. C. Matsumura for communicating unpublished results.

## REFERENCES

- Gundersen, G. *J. Mol. Struct.* 33 (1976) 79.
- Gundersen, G., Jonvik, T. and Seip, R. *Acta Chem. Scand. A* 35 (1981) 325.
- Kroner, J., Nöth, D. and Nöth, H. *Z. Naturforsch. Teil B* 28 (1973) 416.
- Berger, H. O., Kroner, J. and Nöth, H. *Chem. Ber.* 109 (1976) 2266.
- a. Fjeldberg, T., Gundersen, G., Jonvik, T., Seip, H. M. and Sæbø, S. *Acta Chem. Scand. A* 34 (1980) 547; b. Gundersen, G. *Acta Chem. Scand. Submitted.*
- Nöth, H. and Vahrenkamp, H. *Chem. Ber.* 100 (1967) 3353.
- Nöth, H. and Abeler, G. *Chem. Ber.* 101 (1968) 969.
- Aubrey, D. W. and Lappert, M. F. *J. Chem. Soc.* (1959) 2927.
- a. Zeil, W., Haase, J. and Wegmann, L. *Z. Instrumentenk. 74* (1966) 84; b. Bastiansen, O., Graber, R. and Wegmann, L. *Balzers' High Vacuum Report* 25 (1969) 1, Balzers, Lichtenstein.
- Bastiansen, O., Hassel, O. and Risberg, E. *Acta Chem. Scand.* 9 (1955) 232.
- Andersen, B., Seip, H. M., Strand, T. G. and Stølevik, R. *Acta Chem. Scand.* 23 (1969) 3224.
- Gropen, O. and Seip, H. M. *Chem. Phys. Lett.* 25 (1974) 206.
- Clippard, F. B. and Bartell, L. S. *Inorg. Chem.* 9 (1970) 2439.
- Bullen, G. J. and Clark, N. H. *J. Chem. Soc. A* (1970) 992.
- Hess, H. and Reiser, B. *Z. Anorg. Allg. Chem.* 381 (1971) 91.
- Hess, H. *Acta Crystallogr. B* 25 (1969) 2334.
- Weinstock, N. In Niedenzu, K. and Buschbeck, K., Eds., *Gmelin Handbuch der anorganischen Chemie, Ergänzungwerk zur 8. Auflage*, Springer, Berlin-Heidelberg-New York 1975, Vol. 23, Borverbindungen Teil 5, Chapter 3.
- a. Becher, H. J. and Goubeau, J. *Z. Anorg. Allg. Chem.* 268 (1952) 133; b. Becher, H. J. *Spectrochim. Acta* 19 (1963) 575.
- Niedenzu, K., Blick, K. E. and Boenig, I. A. *Z. Anorg. Allg. Chem.* 387 (1972) 107.
- Aubrey, D. W., Lappert, M. F. and Pyszora, H. *J. Chem. Soc.* (1960) 5239.
- Kyker, G. S. and Schram, E. P. *J. Am. Chem. Soc.* 90 (1968) 3678.
- Mido, Y. and Murata, H. *Bull. Chem. Soc. Jpn.* 42 (1969) 3372.
- Goubeau, J., Bessler, E. and Wolff, D. *Z. Anorg. Allg. Chem.* 352 (1967) 285.
- Burch, J. E., Gerrard, W., Goldstein, M., Mooney, E. F. and Willis, H. A. *Spectrochim. Acta* 18 (1962) 1403.



25. a. Sugie, M., Takeo, H. and Matsumura, C. *Chem. Phys. Lett.* 64 (1979) 573; b. Matsumura, C. *Private communication.*
26. a. Briggs, T. S., Gwinn, W. D., Jolley, W. L. and Thorne, L. R. *J. Am. Chem. Soc.* 100 (1978) 7762; b. Gwinn, W. D. *8th Austin Symposium on Gas Phase Molecular Structure 1980*, p. 45.
27. Almenningen, A., Fernholt, L., Fjeldberg, T. and Gundersen, G. *Preliminary results; details on request.*
28. Chang, C. H., Porter, R. F. and Bauer, S. H. *Inorg. Chem.* 8 (1969) 1677.
29. Harschbarger, W., Lee, G., Porter, R. F. and Bauer, S. H. *Inorg. Chem.* 8 (1969) 1683.
30. Coffin, K. P. and Bauer, S. H. *J. Phys. Chem.* 59 (1955) 193.
31. Viswamitra, M. A. and Vaidya, S. N. Z. *Kristallogr.* 121 (1965) 472.
32. Lux, D., Schwarz, W. and Hess, H. *Cryst. Struct. Commun.* 8 (1979) 33.
33. Fusstetter, H., Huffman, J. C., Nöth, H. and Schaeffer, R. *Z. Naturforsch. Teil B* 31 (1976) 1441.
34. Clark, A. H. and Anderson, G. A. *Chem. Commun.* (1969) 1082.
35. Nöth, H., Ullmann, R. and Vahrenkamp, H. *Chem. Ber.* 106 (1973) 1165.
36. Bullen, G. J. and Clark, H. N. *J. Chem. Soc. A* (1969) 404.
37. Harschbarger, W., Lee, G. H., Porter, R. F. and Bauer, S. H. *J. Am. Chem. Soc.* 91 (1969) 551.
38. Huffmann, J. C., Fusstetter, H. and Nöth, H. *Z. Naturforsch. Teil B* 31 (1976) 289.
39. Hess, H. *Acta Crystallogr. B* 25 (1969) 2342.
40. Zettler, F. and Hess, H. *Chem. Ber.* 108 (1975) 2269.
41. Beagley, B. and Hewitt, T. G. *Trans. Faraday Soc.* 64 (1968) 2561.
42. Seip, R., Seip, H. M. and Niedenzu, K. *J. Mol. Struct.* 17 (1973) 361.
43. Seip, R. and Seip, H. M. *J. Mol. Struct.* 28 (1975) 441.
44. Bartell, L. S. and Carroll, B. L. *J. Chem. Phys.* 42 (1965) 3076.

Received September 30, 1980.