Crystallographic Studies of the Boron–Nitrogen Bond in Aminoboranes. Part IV.[1] Crystal and Molecular Structure of (Diphenylmethyleneamino)-dimesitylborane

By **Graham J. Bullen,** Department of Chemistry, University of Essex, Colchester CO4 3SQ

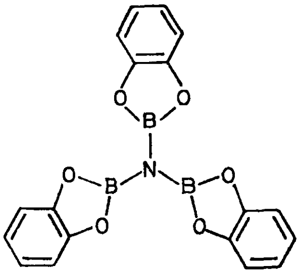
Crystals of the title compound are orthorhombic, $a = 17{\cdot}36$, $b = 29{\cdot}25$, $c = 10{\cdot}12$ Å, space group *Pbca*, $Z = 8$. Their structure was determined from diffractometer *X*-ray intensity data by direct methods and refined by full-matrix least squares to R 0·078 for 608 reflexions. The $>\mathrm{B}\overset{\leftarrow}{-}\mathrm{N}{=}\mathrm{C}<$ system in the molecule has an allene-type geometry with $\mathrm{B}\overset{\leftarrow}{-}\mathrm{N}$ 1·38(2), C=N 1·29(2) Å, and a B–N–C of 173(2)°. Bond orders obtained by MO calculations are: $\mathrm{B}\overset{\leftarrow}{-}\mathrm{N}$ 1·6, C=N 1·8. The mean B–C bond length is 1·59(2) Å. The mesityl and phenyl groups are rotated from the position eclipsed with the $\mathrm{B}\overset{\leftarrow}{-}\mathrm{N}$ or C=N bonds, the torsion angles being: C–C–B–N −51 and −65, and C–C–C–N 29 and 50°.

THE aim of previous papers in this series has been to demonstrate, by determination of stereochemistry, that in aminoboranes there is a significant degree of $\mathrm{B}\overset{\leftarrow}{-}\mathrm{N}$ dative π-bonding. It was shown in particular that in a $>\mathrm{B}\overset{\leftarrow}{-}\mathrm{N}<$ system the environment of the three-co-ordinate nitrogen atom is trigonal planar, the most striking example of this being the completely planar molecule of tri-(1,3,2-benzodioxaborol-2-yl)amine (I).[1]

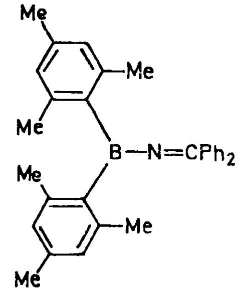
---

[1] Part III, G. J. Bullen and P. R. Mallinson, *J. Chem. Soc.* (*A*), 1970, 2213.

Recently a number of monomeric aldimino- and ketiminoboranes, in which the nitrogen linked to boron is only two-co-ordinate, have been prepared.[2-5] I.r. and n.m.r. measurements indicate that $\mathrm{B}\overset{\leftarrow}{-}\mathrm{N}$ dative π-bonding also occurs in these compounds and that consequently the cumulative $\mathrm{B}\overset{\leftarrow}{-}\mathrm{N{=}C}$ system should be linear as is the isoelectronic $\mathrm{C{=}C{=}C}$ system in allene. Since geometrically the difference between linear $\overset{\leftarrow}{-}\mathrm{N}{=}$ and bent $-\ddot{\mathrm{N}}{=}$ systems is much clearer than the difference between planar $\overset{\leftarrow}{-}\mathrm{N}{<}$ and pyramidal $-\ddot{\mathrm{N}}{<}$, determination of the molecular structure of an aminoborane containing two-co-ordinate nitrogen could provide even more convincing proof of $\mathrm{B}\overset{\leftarrow}{-}\mathrm{N}$ dative π-bonding than from previous studies. It was therefore decided to investigate the crystal structure of (diphenylmethyleneamino)dimesitylborane (II). The i.r. spectrum of this compound shows a band at 1792 cm^{-1}, attributed to the asymmetric stretching frequency of a cumulative $\mathrm{B}\overset{\leftarrow}{-}\mathrm{N{=}C}$ system.[4] By contrast a $\mathrm{B{-}\ddot{N}{=}C}$ system would be expected[6] to have ν(C=N) in the region of 1590—1690 cm^{-1}. Higher stretching frequencies are characteristic of cumulative π-systems [*e.g.* ν_{as}(C=C=C) at 1920—2000,[7] or ν_{as}(C=N=C) at *ca.* 1845 cm^{-1} (ref. 8)]. Molecule (II) offers the possibility of a high B–N bond-order because the donor and acceptor abilities of the nitrogen and boron atoms are confined to one bond.



(I)



(II)

EXPERIMENTAL

Crystal Data.—$\mathrm{C_{31}H_{32}BN}$, $M = 429{\cdot}41$, Orthorhombic, $a = 17{\cdot}36(3)$, $b = 29{\cdot}25(3)$, $c = 10{\cdot}12(2)$ Å, $U = 5139$ Å^3, $D_c = 1{\cdot}11$, $Z = 8$, $D_m = 1{\cdot}08$ (by flotation), $F(000) = 1840$. $\mu = 0{\cdot}72$ cm^{-1} for Mo-K_α radiation, $\lambda = 0{\cdot}7107$ Å. Space group *Pbca* (No. 61) from systematic absences: 0*kl* for *k* odd, *h*0*l* for *l* odd, *hk*0 for *h* odd; Laue symmetry *mmm*.

The crystals were thin flakes parallel to (010) and elongated along *c*. As a precaution against attack by atmospheric moisture (although the substance is reported to be air-stable [4]) they were sealed inside thin-walled glass capillaries for the *X*-ray examination. Unit-cell dimensions were measured from precession photographs (Mo-K_α radiation). *X*-Ray intensities were measured on a Philips PAILRED diffractometer with monochromatised Mo-K_α radiation. The diffraction pattern was weak, statistically significant intensities [with $I > 2\sigma(I)$] being obtained for only 608 independent reflexions out of 2540 measured in the region out to $\sin\theta/\lambda$ 0·5. The intensities of the 00*l* reflexions could not be measured as the crystal was aligned with its *c* axis parallel to the capillary length and this was placed parallel to the ω axis of the diffractometer, but it was clear from *X*-ray photographs that only three 00*l* reflexions of significance were thereby missed. The intensities were corrected for Lorentz and polarisation effects but not for absorption, the linear absorption coefficient being very small.

The sign-determination calculations were carried out at the Atlas Computer Laboratory, Chilton, by use of the '*X*-Ray' programme package, and the least-squares refinement on the University of Essex PDP 10 computer with a programme written by Dr. G. M. Sheldrick. Atomic scattering factors were calculated by the analytic function $f = C + \sum_{i=1}^{4} A_i \exp(-B_i \sin^2\theta/\lambda^2)$, the parameters A, B, and C being taken from ref. 9 for nitrogen, carbon, and boron, and from ref. 10 for hydrogen.

Structure Determination.—The use of Wilson plots to obtain the absolute scale of the *X*-ray intensities and the average temperature factor gave only very approximate values because the plots were curved. Normalised structure factors were calculated and the values of the scale factor and mean temperature factor were adjusted to make the mean E^2 equal to 1. For the $|E|$ values so obtained, 0·8% of the reflexions had $|E| > 3$ and 21% had $|E| > 1$, an unusual distribution since the theoretical prediction is 0·3 and 32% respectively for a random but centrosymmetric arrangement of atoms.[11] This discrepancy is perhaps to be expected because a molecule containing four benzene rings has a considerable degree of order in its atomic arrangement.

Σ_2 Sign relationships were used to determine the signs of 144 reflexions whose $|E|$ values were $>1{\cdot}5$ [these included three reflexions used to define the origin and one reflexion (0,24,0) whose sign was indicated by a number of Σ_1 relationships]. An E map calculated with these signs revealed the nitrogen atom and 30 out of the 31 carbon atom positions. The atoms of phenyl group (ii) (for numbering system see Figure 1) were less distinct in the E map than the other atoms and for this reason three of them were at first placed incorrectly. This relative weakness of phenyl

---

[2] V. A. Dorokhov and M. F. Lappert, *Chem. Comm.*, 1968, 250; *J. Chem. Soc.* (*A*), 1969, 433.

[3] J. R. Jennings, I. Pattison, C. Summerford, K. Wade, and B. K. Wyatt, *Chem. Comm.*, 1968, 250.

[4] C. Summerford and K. Wade, *J. Chem. Soc.* (*A*), 1970, 2010.

[5] M. R. Collier, M. F. Lappert, R. Snaith, and K. Wade, *J.C.S. Dalton*, 1972, 370.

[6] L. J. Bellamy, 'Advances in Infrared Group Frequencies,' Methuen, London, 1968, p. 50.

[7] Ref. 6, p. 65.

[8] B. Samuel and K. Wade, *J. Chem. Soc.* (*A*), 1969, 1742.

[9] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

[10] J. B. Forsyth and M. Wells, *Acta Cryst.*, 1959, **12**, 412.

[11] I. L. Karle, K. S. Dragonette, and S. A. Brenner, *Acta Cryst.*, 1965, **19**, 713.

group (ii) persisted in subsequent Fourier syntheses and is related to the large thermal factors eventually found for these atoms. An electron-density synthesis calculated with 397 reflexions revealed the remaining carbon atom and the boron position and also showed that phenyl group (ii) had been orientated incorrectly. In the subsequent least-squares refinement, hydrogen atoms were incorporated in the calculations. Those in the benzene rings were placed at calculated positions assuming C–H 1·05 Å and those in the methyl groups were located from a difference-Fourier synthesis with subsequent slight adjustment of position to give reasonable bond lengths and angles in the methyl group. By use of individual isotropic temperature factors and unit weights, R was thus reduced to 0·092 for the 608 reflexions. It was not considered worthwhile to refine the temperature factors of all boron, nitrogen, and carbon atoms anisotropically since this would have produced 299 variables to be refined with only 608 reflexions. However it was noted that the temperature factors of the carbon atoms in phenyl group (ii) were large, with $\overline{u^2}$ up to 0·13 Å^2, and furthermore when anisotropy was introduced for these atoms, refinement showed it to be considerable. The possibility was considered that the cause of the large temperature factors (and large anisotropy) of this group of atoms was that the position of the group was disordered, possibly by rotation around the C(31)–C(7) bond. To test this a difference-Fourier synthesis, from which atoms C(8)—(12) and H(8)—(12) were omitted, was examined for peaks in positions other than those already postulated. None was found but the peaks present were considerably spread out, in agreement with the high temperature factors. The hypothesis of disorder was therefore rejected and it was concluded that the high temperature factors represent a real vibration effect. Support for this was provided by the fact that the maximum vibrations of atoms C(7)—(12) lay in approximately the same direction [parallel to the C(9) · · · C(11) line] and that the thermal parameters increased in the order C(7) < [C(8), C(12)] < [C(9), C(10), C(11)]. This suggests that this phenyl group is undergoing large oscillations about an axis perpendicular to the ring and lying outside it, probably in the region of C(31). The connexion between this and the packing of the molecules is discussed on p. 862.

It was therefore considered necessary to retain anisotropic temperature factors for atoms C(7)—(12) in carrying out four further cycles of full-matrix least-squares refinement but, in order to reduce the number of variables, all other atoms were refined isotropically (except hydrogen for which no parameters were refined). The function minimised was $\Sigma w\Delta^2$ where $\Delta = |F_o| - |F_c|$. The weighting scheme $w = 1$ for $|F_o| \leqslant A$ and $w = (A/|F_o|)^2$ for $|F_o| > A$ was used, A being ultimately given the value 85 on absolute scale, to produce similar mean values of $w\Delta^2$ for ranges of increasing $|F_o|$ or sin θ/λ. During this refinement the temperature factors of C(7), C(8), and C(10) became non-positive definite and their values had to be fixed during the final cycle of refinement. In this cycle all parameter shifts were $<0{\cdot}1\sigma$. The final R is 0·078 for 608 reflexions, and R' [$= (\Sigma w\Delta^2/\Sigma w|F_o|^2)^{\frac{1}{2}}$] is 0·097.

RESULTS AND DISCUSSION

Final atomic co-ordinates and thermal vibration parameters are listed in Tables 1 and 2. The co-ordinates and thermal parameters used for the hydrogen atoms are given in Table 3. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20653 (5 pp., 1 microfiche).* Bond lengths and bond angles are given in Figure 1 together with their estimated standard deviations calculated by use of the full covariance matrix. The molecular shape is shown in Figure 2.

TABLE 1

Fractional atomic co-ordinates (×10^4) and mean-square amplitudes of thermal vibration (Å^2 × 10^3) with estimated standard deviations in parentheses

	x/a	y/b	z/c	$\overline{u^2}$
B	948(15)	1251(8)	1755(24)	43(8)
N	1272(9)	1672(5)	1512(14)	42(5)
C(1)	1333(11)	2504(8)	1652(18)	47(6)
C(2)	1541(12)	2881(7)	826(21)	57(7)
C(3)	1218(14)	3306(8)	1227(23)	65(7)
C(4)	726(12)	3340(7)	2255(22)	61(7)
C(5)	542(13)	2953(8)	3012(21)	64(7)
C(6)	840(11)	2517(8)	2739(20)	58(7)
C(7)	2390(15)	1997(7)	604(27)	*
C(8)	2972(17)	2240(8)	930(32)	*
C(9)	3719(20)	2183(10)	512(46)	*
C(10)	3772(24)	1921(18)	−657(47)	*
C(11)	3168(29)	1752(14)	−1236(35)	*
C(12)	2456(20)	1740(9)	−585(27)	*
C(13)	1207(12)	978(6)	3035(12)	37(6)
C(14)	623(13)	779(7)	3815(23)	54(7)
C(15)	797(12)	516(6)	4873(20)	41(6)
C(16)	1554(12)	425(7)	5218(21)	50(7)
C(17)	2144(13)	606(7)	4413(23)	62(8)
C(18)	1952(11)	885(6)	3409(19)	32(6)
C(19)	371(12)	1091(6)	641(19)	36(5)
C(20)	555(13)	698(7)	−100(21)	51(7)
C(21)	72(13)	530(7)	−1102(24)	62(8)
C(22)	−622(13)	737(8)	−1347(23)	61(7)
C(23)	−830(12)	1118(7)	−631(20)	48(6)
C(24)	−319(12)	1289(6)	349(18)	35(6)
C(25)	−212(14)	876(7)	3564(23)	67(8)
C(26)	1773(14)	113(8)	6345(27)	90(9)
C(27)	2625(13)	1074(8)	2568(24)	77(8)
C(28)	1323(13)	444(7)	68(22)	68(7)
C(29)	−1128(16)	561(8)	−2449(30)	110(10)
C(30)	−580(11)	1717(6)	1091(19)	49(6)
C(31)	1641(11)	2040(6)	1218(18)	32(6)

* See Table 2 for anisotropic thermal parameters.

TABLE 2

Components U_{ij} of thermal vibration tensors (Å^2 × 10^2). Estimated standard deviations are given only for components which were refined in the final least-squares cycle

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(7)	6	2	11	3	4	−1
C(8)	7	3	19	7	4	0
C(9)	6(2)	12(3)	29(5)	11(3)	−6(3)	2(2)
C(10)	8	20	15	10	10	5
C(11)	19(4)	21(4)	11(3)	11(3)	2(3)	7(4)
C(12)	15(3)	6(2)	8(2)	2(2)	6(2)	2(2)

π-Bonding between the boron and nitrogen atoms producing a $\mathrm{B}\overset{\leftarrow}{=}\mathrm{N}{=}\mathrm{C}$ system analogous to the C=C=C in allene is indicated by the following features of the molecular geometry: the B–N–C angle is close to 180°, the B–N bond is short, and the planar groupings C(13)–C(19)–B–N and C(1)–C(7)–C(31)–N are very nearly mutually perpendicular (dihedral angle 86°, see Table 4 for equations of planes). The mesityl groups are pre-

---

* For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20.

vented by steric hindrance from being coplanar with the neighbouring trigonal grouping at the boron atom (Figure 2). Likewise the phenyl groups are not coplanar with the trigonal grouping around C(31). The torsion angles of these groups (measured as the angles between pairs of mean planes listed in Table 4) are: C(18)–C(13)–B–N −51, C(24)–C(19)–B–N −65, C(6)–C(1)–C(31)–N 29°, and C(12)–C(7)–C(31)–N 50°. The inequality of the torsion angles of the two mesityl groups (or the two phenyl groups), *i.e.* the failure of the molecule to possess a C_2 symmetry axis along the B–N bond [see Figure 2(b)], must be the result of inter- rather than intra-molecular forces. The twist of the four benzene rings about the bonds joining them to C(31) or boron prevents them from having π-electron systems in common with the C(31)–N or B–N bonds.

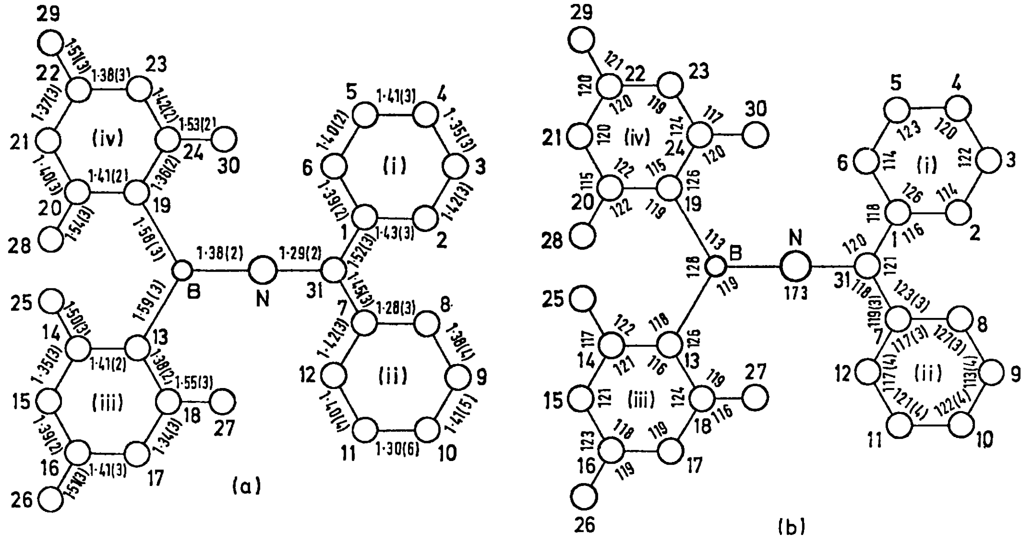


FIGURE 1 (a) Bond lengths (Å) with estimated standard deviations in parentheses and (b) bond angles (°). All atoms are carbon unless marked otherwise, and the atom numbering system is shown. Estimated standard deviations are 2° for all bond angles, except those at ring (ii) which are marked

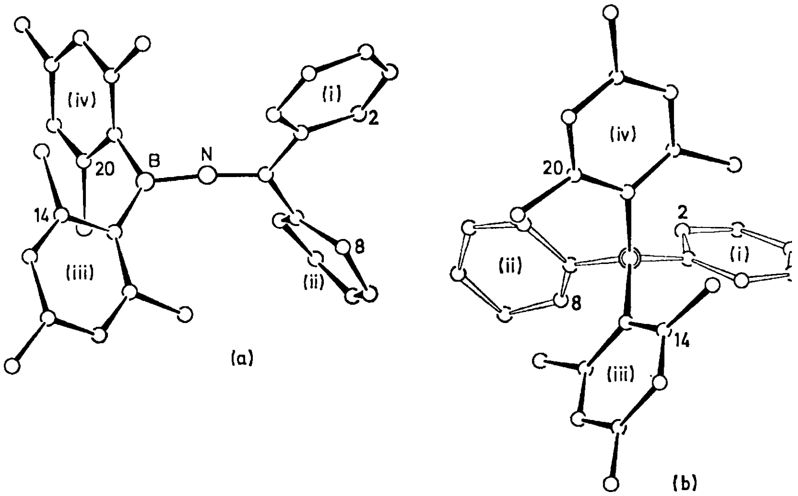


FIGURE 2 The molecule viewed in directions (a) perpendicular to and (b) along the B–N bond. The double circle in the centre of (b) represents a superposition of the three atoms B, N, and C(31)

Length and Order of the B–N *Bond.*—The B–N bond length (1·38 Å) is one of the shortest found in aminoboranes [*cf.* 1·40 and 1·43 in Me_2NBMe_2,[12] 1·41 in *B*-trichloroborazole,[13] and 1·387 and 1·407 Å in $(Me_2NBCH_2)_3$ [14]]. The bond order corresponding to this length was calculated using the LCAO method as for other molecules examined in this series.[1,12] Solution of the equations $[H_{kj} - ES_{kj}][c_j] = 0$ gave the eigenvalues E_1 and E_2 and the corresponding eigenvectors $[c_j]_1$ and $[c_j]_2$ (Table 5). The coulomb, overlap, and exchange integrals were derived as previously,[1] with the values S_{BN} 0·243 and H_{BN} −4·89 eV corresponding to the bond

---

[12] G. J. Bullen and N. H. Clark, *J. Chem. Soc.* (*A*), 1970, 992.

[13] D. L. Coursen and J. L. Hoard, *J. Amer. Chem. Soc.*, 1952, **74**, 1742.

[14] H. Hess, *Acta Cryst.*, 1969, **B25**, 2334.

TABLE 3

Fractional co-ordinates ($\times 10^3$) assigned to hydrogen atoms, numbered according to the carbon atom to which they are attached. For H(9), H(10), and H(11) $\overline{u^2}$ is 0·16 Å^2, for all others 0·09 Å^2

	x/a	y/b	z/c
H(2)	188	285	−2
H(3)	140	359	74
H(4)	46	366	248
H(5)	16	300	381
H(6)	71	224	338
H(8)	291	249	180
H(9)	420	231	95
H(10)	429	189	−128
H(11)	319	157	−211
H(12)	200	155	−104
H(15)	33	39	548
H(17)	271	55	466
H(21)	23	22	−150
H(23)	−137	127	−75
H(25a)	−45	66	282
H(25b)	−30	122	330
H(25c)	−54	82	445
H(26a)	136	−17	636
H(26b)	231	−2	620
H(26c)	172	29	725
H(27a)	275	141	288
H(27b)	252	107	157
H(27c)	314	89	277
H(28a)	178	68	14
H(28b)	132	26	95
H(28c)	145	23	−72
H(29a)	−111	81	−322
H(29b)	−170	59	−208
H(29c)	−99	24	−277
H(30a)	−7	186	162
H(30b)	−96	163	183
H(30c)	−79	196	49

TABLE 4

Equations of mean planes through sets of atoms and distances of these and other atoms from the plane (in square brackets). Co-ordinates and distances are in Å

Plane (i):

C(1)—(6) $\quad 0{\cdot}780X + 0{\cdot}181Y + 0{\cdot}599Z = 4{\cdot}129$

[C(1) 0·005, C(2) −0·015, C(3) 0·017, C(4) −0·008, C(5) −0·003, C(6) 0·004]

Plane (ii):

C(7)—(12) $\quad -0{\cdot}209X + 0{\cdot}810Y - 0{\cdot}548Z = 3{\cdot}595$

[C(7) −0·066, C(8) 0·118, C(9) −0·057, C(10) −0·048, C(11) 0·092, C(12) −0·039]

Plane (iii):

C(13)—(18) $\quad 0{\cdot}013X + 0{\cdot}805Y + 0{\cdot}593Z = 4{\cdot}151$

[C(13) 0·000, C(14) −0·014, C(15) 0·006, C(16) 0·015, C(17) −0·029, C(18) 0·022, C(25) 0·046, C(26) −0·039, C(27) −0·023]

Plane (iv):

C(19)—(24) $\quad 0{\cdot}447X + 0{\cdot}583Y - 0{\cdot}679Z = 1{\cdot}703$

[C(19) 0·004, C(20) −0·014, C(21) 0·014, C(22) −0·003, C(23) −0·007, C(24) 0·007, C(28) 0·033, C(29) 0·062, C(30) 0·024]

Plane (v):

B, N, C(13), C(19) $\quad -0{\cdot}749X + 0{\cdot}427Y + 0{\cdot}507Z = 1{\cdot}212$

[B 0·016; N, C(13), and C(19) −0·005; C(31) −0·177]

Plane (vi):

C(31), N, C(1), C(7) $\quad 0{\cdot}455X - 0{\cdot}072Y + 0{\cdot}888Z = 1{\cdot}996$

[C(31) −0·037, N 0·013, C(1) and C(7) 0·012, B 0·065]

length 1·38 Å. With the two π-electrons occupying the bonding orbital E_2, the π-bond order p_{BN} calculated from the eigenvectors taking into account overlap[15] is 0·59. The π-charge densities are ρ_N 1·83 and ρ_B 0·17 e. The total boron–nitrogen bond order ($\sigma + \pi$) is therefore 1·59, which is slightly greater than that found[12] for Me_2NBMe_2 (1·57) reflecting the shorter bond length in $Ph_2C{:}NB(C_6H_2Me_3)_2$. This degree of π-bonding is considerably less than in ethylene and allene and is more comparable to that in benzene (bond order 1·67). An analogous LCAO calculation for the C=N bond in $Ph_2C{:}NB(C_6H_2Me_3)_2$ gives p_{CN} 0·84, ρ_N 1·56, and ρ_C = 0·44 e. The C=N length is similar to that in a number of oximes, *e.g. p*-chlorobenzaldoxime (1·26 and 1·27 Å).[16]

TABLE 5

Eigenvalues E_i and eigenvectors $[c_j]_i$ for the B–N group

i	E_i (eV)	$(c_B)_i$	$(c_N)_i$
1	−7·18	1·0122	−0·4354
2	−14·76	0·1953	0·9344

Other Bond Lengths and Bond Angles.—The mean B–C length [1·59(2) Å] is similar to the values usually found.[14,17] The mean C–C length in the benzene rings (i), (iii), and (iv) is 1·390(6) Å. The bond lengths in ring (ii) cover a wide range and are clearly unreliable, in some cases having very large σ. The mean C(ring)–C(methyl) length is 1·52(1) Å.

The slight deviation of the B–N–C angle from 180° results mainly from atom C(31) lying 0·18 Å away from the C(13)–C(19)–B–N planar (Table 4); the B–N–C(31) plane is almost perpendicular to the C(13)–C(19)–B–N plane (dihedral angle 87°).

Although the three bond angles at C(31) are equal within experimental error, those at the boron atom show a considerable departure from the ideal 120°. The C–B–C angle is probably enlarged in order to avoid interference between the mesityl groups, but even so some of the non-bonded contacts are very close, *e.g.* C(19) · · · C(25) 3·19 and C(13) · · · C(28) 3·39 Å. Other bond angles are unexceptional.

The mesityl groups are planar, the deviations of the methyl carbon atoms from the mean plane of the ring being in all cases $<2{\cdot}3\sigma$ (Table 4). Although phenyl ring (i) is planar and regular, ring (ii) is considerably distorted [Figure 1(a) and Table 4] and has large thermal vibrations. The thermal parameters in Table 2 correspond to root-mean-square amplitudes of vibration up to 0·6 Å, whereas the atoms of ring (i) have root-mean-square amplitudes no larger than 0·26 Å. The reason for the large (and very anisotropic) thermal vibrations of ring (ii) is probably that it lies in a region of the crystal lattice where the molecules are very loosely packed. The number of C · · · C intermolecular contacts

---

[15] B. H. Chirgwin and C. A. Coulson, *Proc. Roy. Soc.*, 1950, *A*, **201**, 196.

[16] B. Jerslev, *Nature*, 1957, **180**, 1410.

[17] *Chem. Soc. Special Publ.*, No. 18, 1965, p. *S*14*s*.

up to 4·2 Å made by the atoms of rings (i) and (ii) are as follows:

n	C(*n*)	C(6 + *n*)
1	3	1
2	3	1
3	7	3
4	9	4
5	12 *	3
6	4	6

* One of the 12 contacts made by C(5) is to a nitrogen atom.

With the exception of C(6) and C(12), each atom of ring (ii) makes considerably fewer contacts than the corresponding atom of ring (i). Moreover, whereas three atoms of ring (i) make contacts as short as 3·55—3·57 Å, no atom of ring (ii) has a contact <3·72 Å. The forces holding ring (ii) in place are clearly weaker than those holding ring (i). Such a disparity in environment does not occur between the two mesityl groups which show only minor differences in the number of contacts made by corresponding carbon atoms. The shortest intermolecular $CH_3 \cdots CH_3$ contact is 3·82 Å and the shortest $CH_3 \cdots CH$ is 3·80 Å.

A near-linear configuration has also been found for $Al \leftarrow N{=}C$ (angle at nitrogen 167°) in $LiAl(N{=}CBu^t_2)_4$[18] which again has a high-frequency azomethine stretching absorption (1700 cm^{-1}). The wider implication of this and the present work is that allene-type geometries will apply to $M{-}N{=}CR_2$ systems when M is an electron acceptor and a high azomethine stretching frequency is observed. Compounds satisfying these conditions are known for M = Be,[19] B, C,[8] and Al.[20]

I thank Drs. K. Wade and R. Snaith for supplying a sample of the aminoborane, the University of Essex Computing Centre and the Atlas Computer Laboratory, Chilton, for facilities, Dr. G. M. Sheldrick for making his computer programme available, N. Lewis for the preparation of diagrams, and the Department of Physical Chemistry, University of Cambridge, for its hospitality while this paper was being prepared.

[2/2548 *Received*, 10*th November*, 1972]

---

[18] H. M. M. Shearer, R. Snaith, J. D. Sowerby, and K. Wade, *Chem. Comm.*, 1971, 1275.

[19] C. Summerford, K. Wade, and B. K. Wyatt, *J. Chem. Soc.* (*A*), 1970, 2016.

[20] R. Snaith, C. Summerford, K. Wade, and B. K. Wyatt, *J. Chem. Soc.* (*A*), 1970, 2635.