Crystallographic Studies of the Boron–Nitrogen Bond in Aminoboranes. Part 5.[1] The Crystal and Molecular Structure of 1,5,9-Triaza-13-boratricyclotridecane

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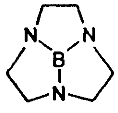
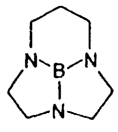
Crystals of the title compound are orthorhombic, a = 8.69(1), b = 14.07(1), c = 8.48(1) Å, space group $P2_12_12_1$, and Z = 4. The atomic positions have been determined from diffractometer X-ray intensity data by the tangent refinement method and refined by full-matrix least-squares to R 0.050 for 414 reflections. The molecular symmetry is approximately C_{3v} ($3m$). The BN_3 system is almost planar but the carbon atoms lie out of this plane, by 0.3—0.4 Å above for atoms in the 3-, 7-, and 11-positions and by smaller amounts below for the remaining carbon atoms. Mean bond lengths are: B–N 1.431(6), C–N 1.446(4), C–C 1.521(5) Å and the B–N bond order obtained by molecular-orbital calculations is 1.4.

PREVIOUS papers in this series have given stereochemical evidence for the possession of considerable π character by the B–N bond in the environments $>$B–N$<$ or $>$B–N=C$<$ involving three- or two-co-ordinate nitrogen atoms respectively.[1-3] π Bonding in molecules containing three-co-ordinate nitrogen leads to essentially planar molecules such as triazaboradecalin[2] which is stereochemically more akin to naphthalene than to decalin. Recently, Richman *et al.*[4] have prepared a series of new tricyclic tris(amino)boranes. Their spectroscopic evidence (i.r., n.m.r., and mass spectra) suggests that among these (1) is dimeric in both gaseous and solid states, the boron and one nitrogen atom probably being four-co-ordinate, (2) is monomeric in the gas but probably dimeric in the solid, while (3) is monomeric in both states. Richman *et al.* suggest that the fusion of three five-membered rings in (1) constrains the nitrogen atoms to a pyramidal geometry and this, by leaving the lone-pair electrons on nitrogen stereochemically active, leads to dimerisation, whereas the larger rings in (3) allow a more nearly planar nitrogen geometry conducive to B–N π bonding and hence stabilisation of the monomer. The crystal-structure analysis of (3), presented here, confirms that the molecule is monomeric with a substantial degree of B–N π-bond character and a nitrogen geometry that is close to planar.



(1)



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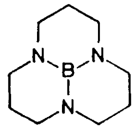

(3)

EXPERIMENTAL

Crystal Data.—$C_9H_{18}BN_3$, M = 179.07, Orthorhombic, a = 8.69(1), b = 14.07(1), c = 8.48(1) Å, U = 1 037 Å^3, $Z = 4$, D_c = 1.147 g cm^{-3}, $F(000) = 392$, μ = 0.75 cm^{-1} for Mo-K_α radiation, λ = 0.710 7 Å. Space group $P2_12_12_1$ (no. 19) from systematic absences of X-ray reflections: $h00$ when h is odd, $0k0$ when k is odd, $00l$ when l is odd; Laue symmetry mmm.

Crystals were sealed inside thin-walled glass capillaries for the X-ray examination because they are slightly hygroscopic. Unit-cell dimensions were measured from precession photographs (Mo-K_α radiation) and on a Philips PAILRED diffractometer, the latter also being used for intensity measurements (monochromatised Mo-K_α radiation). 823 Reflections, with $(\sin\theta)/\lambda$ up to 0.58, were measured at 20—25 °C but the diffraction pattern was weak and only 422 reflections gave significant intensities, satisfying $I > 2\sigma(I)$. The intensities were corrected for Lorentz and polarisation effects but not for absorption, the linear absorption coefficient being very small.

The phase-determination calculations and the least-squares refinement were carried out on the University of Essex PDP 10 computer with programs written by Professor G. M. Sheldrick. Atomic scattering factors were calculated by the analytic function $f = C + \sum_{i=1}^{n} A_i\exp[(-B_i\sin^2\theta)/\lambda^2]$, the parameters A, B, and C being taken from ref. 5 for nitrogen, carbon, and boron (n = 4), and from ref. 6 for hydrogen (n = 2).

As few crystals were available and they are susceptible to hydrolysis, their density was not measured. Assuming that there are four molecules in the unit cell gives a calculated density (1.147 g cm^{-3}) very close to the density of triazaboradecalin (1.156 g cm^{-3}).[2]

Structure Determination.—The structure was solved by the tangent refinement method[7] applied to 163 reflections with $|E| > 1.0$. The origin and the enantiomorph were defined by assigning phase angles of 90° to reflections 130 and 403 and zero to reflections 490 and 085. The E map calculated after tangent refinement showed the positions of all atoms other than hydrogen.

The positions and anisotropic temperature factors of boron, nitrogen, and carbon atoms were subjected to least-squares refinement. Hydrogen atoms were included in the calculations, their positions being fixed so that the C–H bond lengths are approximately 1.05 Å and the carbon atoms are tetrahedrally co-ordinated. The function minimised was $\Sigma w\Delta^2$ where $\Delta = |F_o| - |F_c|$ and the weight $w = (|F_o|/A)^2$ for $|F_o| \leqslant A$ or $w = (A/|F_o|)^2$ for $|F_o| > A$, A being given the value 15 in the final stages of the refinement. With this weighting scheme, average $w\Delta^2$ for groups of reflections were similar over the whole range of $|F_o|$ and of $(\sin\theta)/\lambda$. 414 Reflections were used in the refinement and eight weak reflections which persistently gave large Δ were omitted. The final R is 0.050 for 414 reflections and R' $[= (\Sigma w\Delta^2/\Sigma w|F_o|^2)^{\frac{1}{2}}]$ is 0.042. In the last cycle of refinement all parameter shifts were less than 0.1 σ.

RESULTS

Final atomic co-ordinates are listed in Table 1, the numbering of the atoms and the molecular shape being shown in Figure 1. The co-ordinates used for the hydrogen atoms are given in Table 2. Observed and calculated structure factors and thermal parameters are listed in Supplementary Publication No. SUP 22943 (7 pp.).* Bond lengths are given in Table 3 and bond angles in Figure 2 together with their estimated standard deviations. A rigid-body libration analysis of the molecule, in which the molecular vibrations are treated in terms of three tensors, $\boldsymbol{T}$ for translation, $\boldsymbol{L}$ for libration, and $\boldsymbol{S}$ for correlations of translation and libration,[8] gave the results in Table 4(*a*). The $\boldsymbol{L}$ tensor transformed to orthogonal molecular axes is shown in Table 4(*b*), these axes being chosen so that X is the normal to the mean molecular plane, Y is in the mean plane and perpendicular to the N(1) $\cdots$ N(2) line, and Z is perpendicular to X and Y. When referred to these axes $\boldsymbol{L}$ is effectively diagonalised as the L_{ij} $(i \neq j)$ are not significantly different from zero, and hence the molecular motion can be considered in terms of libration about the three molecular axes. The libration amplitudes are quite considerable and the weakness of the X-ray diffraction pattern, noted above, is attributable to this. The largest libration (root-mean-square amplitude 7.3°) is that about the normal to the molecular plane. The bond lengths must be increased by 0.014—0.017 Å to allow for the effect of the molecular librations [9] [corrected values are in Table 3(*b*)].

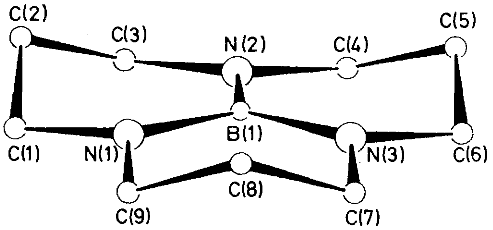

FIGURE 1 Molecular shape and numbering of the atoms

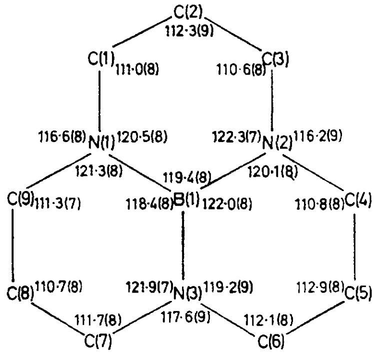

FIGURE 2 Bond angles (°) with estimated standard deviations in parentheses

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

TABLE 1

Fractional atomic co-ordinates (× 10^4) with estimated standard deviations in parentheses

Atom	*x/a*	*y/b*	*z/c*
B(1)	3 701(10)	3 908(6)	1 259(11)
N(1)	3 381(7)	4 141(4)	−360(8)
N(2)	2 781(8)	3 238(5)	2 034(8)
N(3)	5 012(8)	4 307(5)	1 973(8)
C(1)	2 220(13)	3 640(7)	−1 213(10)
C(2)	949(12)	3 304(8)	−118(14)
C(3)	1 561(11)	2 732(6)	1 244(14)
C(4)	3 236(14)	2 875(6)	3 551(11)
C(5)	4 173(15)	3 592(8)	4 426(10)
C(6)	5 491(13)	3 966(8)	3 480(13)
C(7)	6 061(10)	4 888(7)	1 118(14)
C(8)	5 273(12)	5 397(6)	−250(15)
C(9)	4 420(11)	4 701(7)	−1 267(10)

TABLE 2

Fractional co-ordinates (× 10^3) assigned to hydrogen atoms, all of which were given thermal parameters $\bar{u}^2$ equal to 0.1 Å^2

Atom	*x/a*	*y/b*	*z/c*
H(11) *	271	305	−178
H(12)	176	409	−208
H(21)	34	390	31
H(22)	15	290	−76
H(31)	198	208	82
H(32)	67	259	204
H(41)	388	225	338
H(42)	224	270	419
H(51)	459	328	547
H(52)	346	416	478
H(61)	632	343	332
H(62)	603	452	409
H(71)	696	447	68
H(72)	655	539	188
H(81)	610	575	−94
H(82)	449	591	18
H(91)	521	425	−184
H(92)	381	507	−215

* Hydrogen atoms H(*n*1) and H(*n*2) are attached to carbon atom C(*n*).

TABLE 3

Bond lengths (Å) with estimated standard deviations in parentheses

(*a*) Bond lengths from the least-squares refinement

B(1)–N(1)	1.439(9)	C(1)–C(2)	1.518(13)
B(1)–N(2)	1.400(10)	C(2)–C(3)	1.505(12)
B(1)–N(3)	1.407(10)	C(4)–C(5)	1.493(14)
		C(5)–C(6)	1.494(13)
		C(7)–C(8)	1.525(13)
C(1)–N(1)	1.428(10)	C(8)–C(9)	1.500(12)
C(3)–N(2)	1.442(11)		
C(4)–N(2)	1.440(9)		
C(6)–N(3)	1.427(11)		
C(7)–N(3)	1.423(10)		
C(9)–N(1)	1.424(10)		

(*b*) Corrected for molecular oscillations

B(1)–N(1)	1.453	C(1)–C(2)	1.532
B(1)–N(2)	1.415	C(2)–C(3)	1.520
B(1)–N(3)	1.424	C(4)–C(5)	1.510
Mean	1.431(6)	C(5)–C(6)	1.509
		C(7)–C(8)	1.540
C(1)–N(1)	1.445	C(8)–C(9)	1.517
C(3)–N(2)	1.459	Mean	1.521(5)
C(4)–N(2)	1.454		
C(6)–N(3)	1.441		
C(7)–N(3)	1.438		
C(9)–N(1)	1.438		
Mean	1.446(4)		

DISCUSSION

The molecular structure of triazaboratricyclotridecane shows considerable similarity to that of triazaboradecalin.[2] The BN_3 grouping is very nearly planar (Table 5) and the six carbon atoms bonded directly to nitrogen also lie close to this plane (0.15—0.21 Å below it). However, as in triazaboradecalin, the central carbon atoms in the trimethylene bridges [C(2), C(5), and C(8)] deviate from the BN_3 plane by larger amounts (0.32—0.41 Å). They also lie on the opposite side of the BN_3 plane from the other six carbon atoms. The approximate molecular symmetry is thus C_{3v} ($3m$) with each mirror plane containing one B–N bond (see Figure 1).

TABLE 4

Molecular vibration tensors with their origin (chosen to make $\boldsymbol{S}$ symmetric) at (0.364, 0.395, 0.098)

(*a*) Referred to the crystallographic axes

$$\boldsymbol{T} = \begin{pmatrix} 0.040(3) & 0.000(3) & -0.004(2) \\ & 0.042(4) & -0.001(3) \\ & & 0.050(3) \end{pmatrix} \text{Å}^2$$

$$\boldsymbol{L} = \begin{pmatrix} 0.008\,7(9) & -0.005\,5(7) & -0.003\,2(6) \\ & 0.010\,5(7) & 0.001\,3(6) \\ & & 0.007\,8(10) \end{pmatrix} \text{radian}^2$$

$$\boldsymbol{S} = \begin{pmatrix} 0.000\,4(11) & -0.001\,0(7) & 0.002\,7(10) \\ & -0.000\,9(11) & -0.000\,5(8) \\ & & 0.000\,4(12) \end{pmatrix} \text{radian Å}$$

(*b*) Referred to molecular axes as defined in the text

$$\boldsymbol{L} = \begin{pmatrix} 53.2 & -3.0 & 2.0 \\ & 11.3 & 1.2 \\ & & 24.2 \end{pmatrix} \text{degree}^2$$

In conformity with this molecular symmetry, all bonds of the same chemical type (*e.g.* all C–N bonds) are of equal length within experimental error. The shortness of the B–N bonds, mean length 1.431(6) Å [*cf.* 1.421 Å in triazaboradecalin [2] and 1.438 Å in tri(benzodioxaborolyl)amine [3]], and the nearly trigonal planar configuration of the nitrogen atoms indicate π bonding between boron and nitrogen. The π-bond order in the BN_3 grouping was calculated by the LCAO method as for triazaboradecalin.[2] Solution of the equations $[H_{kj} - ES_{kj}][c_j] = 0$ gave the eigenvalues E_1—E_4 and the corresponding eigenvectors (Table 6). The coulomb, exchange, and overlap integrals appropriate to the bond length 1.431 Å were derived as previously:[2] $H_{BB} = -8.53$, $H_{NN} = -14.49$, $H_{BN} = -4.53$, $H_{NN'} = -0.254$ eV,* $S_{BN} = 0.225$, $S_{NN'} = 0.010$. With the six π electrons occupying the bonding orbital E_4 and the two non-bonding orbitals E_2 and E_3, the π-bond order p_{BN} calculated from the eigenvectors taking into account overlap [10] is 0.43. The π-charge densities are ρ_N 1.90 and ρ_B 0.29 e. The total boron–nitrogen bond order ($\sigma + \pi$) is therefore 1.43.

TABLE 5

Distances of the atoms from the mean plane of the BN_3 grouping: $-0.5748x + 0.7519y + 0.3228z = 2.602\,7$; co-ordinates and distances are in Å units

Atom	B(1)	N(1)	N(2)	N(3)
Distance	0.028	−0.009	−0.010	−0.010
Atom	C(1)	C(2)	C(3)	
Distance	−0.193	0.387	−0.152	
Atom	C(4)	C(5)	C(6)	
Distance	−0.205	0.324	−0.197	
Atom	C(7)	C(8)	C(9)	
Distance	−0.153	0.405	−0.184	

Other Bond Lengths and Bond Angles.—The six C–N bond lengths, mean 1.446(4) Å, are equal within experimental error and slightly shorter than the standard length,[11] 1.472 Å, as might be expected for $C(sp^3)$–$N(sp^2)$ bonds. The six C–C bond lengths, mean 1.521(5) Å, are also equal within experimental error and shorter than the standard value,[12] 1.54 Å. The mean lengths for these two types of bond are very similar to those found in triazaboradecalin: C–N 1.452 Å, C–C 1.517 Å.

The bond angles (Figure 2) are much as expected, those at boron and nitrogen atoms being close to 120° while those at carbon are in the range 111—113°. At the nitrogen atoms the exocyclic angles tend to be smaller than the endocyclic angles, the differences being significant at N(1) and N(2) but not at N(3).

TABLE 6

Eigenvalues E_i and eigenvectors $[c_j]_i$ for the BN_3 grouping (j = 1, 2, or 3 for the three nitrogen atoms and j = B for boron)

i	E_i (eV)	$(c_1)_i$	$(c_2)_i$	$(c_3)_i$	$(c_B)_i$
1	−5.02	0.3633	0.3633	0.3633	−1.0553
2	−14.38	0.7106	−0.7106	0	0
3	−14.38	0.4103	0.4103	−0.8206	0
4	−15.24	0.5020	0.5020	0.5020	0.2474

The arrangement of the molecules in the unit cell is shown in Figure 3. The planes of neighbouring molecules are steeply inclined to each other as a result of the tilt of the molecules with respect to the three screw axes. The angles between the mean planes of pairs of adjacent molecules mutually related by the screw axes parallel to a, b, and c are respectively 70°, 82°, and 38°. As a result the closest intermolecular contacts (<4 Å, hydrogen atoms not counted) always involve carbon atoms, and the majority of them occur between those molecules mutually related by the screw axes parallel to the shorter unit-cell dimensions a or c. The shortest contacts of each type are B $\cdots$ CH_2 3.80, N $\cdots$ CH_2 3.76, and CH_2 $\cdots$ CH_2 3.90 Å. Every atom in the molecule makes one or two contacts within the range

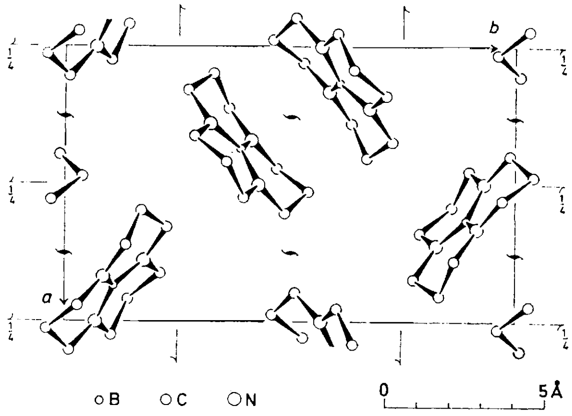

FIGURE 3 Projection of the crystal structure on (001)

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* Throughout this paper: 1 eV ≈ 1.60 × 10^{-19} J.

3.8—4.0 Å with the exception of C(7) whose closest contact is at 4.07 Å. There are no B · · · N or N · · · N contacts shorter than 4.3 Å.

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