

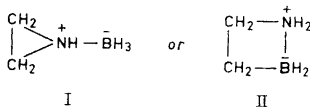
## The Crystal and Molecular Structure of Aziridine Borane

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The reaction between borane and aziridine has been shown to yield the addition compound aziridine borane,  $C_2H_3BN$ . The unit cell of aziridine borane is orthorhombic with  $a=8.44$ ,  $b=8.99$ , and  $c=5.65$  Å. The space group is  $Pmnb$  with 4 molecules in the cell. The crystal structure was solved by Patterson and direct methods and the molecular structure refined to  $R=8.7\%$ . The molecules are bonded together in chains by weak charge-transfer bridges.

Alkylamine boranes are strongly reducing substances and therefore of potential interest as radical scavengers and radioprotective agents. During the synthesis of such substances Åkerfeldt, Wahlberg and Hellström<sup>1</sup> found that aziridine and certain of its derivatives gave addition compounds with borane that behaved differently from normal secondary amine borane complexes. The reaction with aziridine could lead to different structural configurations, e.g.



Some preliminary NMR, IR, dipole measurements and chemical evidences favoured formula II but later studies with  $^{11}\text{B}$ -NMR favoured formula I. A crystallographic investigation was carried out to ascertain which of the two products had been formed.

## EXPERIMENTAL

The material was obtained from Dr. Åkerfeldt of the Research Institute of National Defence, Sweden. It crystallizes in transparent flakes from a mixture of benzene and cyclohexane. The crystals are soft and not stable in air. Cell parameters were determined using a PAILRED automatic diffractometer and  $\text{MoK}\alpha$ -radiation ( $\lambda=0.7107$  Å).

$$\begin{array}{l}
 a = 8.44 (\pm 1) \text{ \AA} \\
 b = 8.99 (\pm 1) \text{ \AA} \\
 c = 5.65 (\pm 1) \text{ \AA} \\
 \alpha = \beta = \gamma = 90^\circ
 \end{array}$$

This gives  $D_x = 0.88 \text{ g cm}^{-3}$  with  $Z = 4$ ;  $D_m$  is  $0.90 \text{ g cm}^{-3}$ . From the systematic absences the space group could be either  $Pc2_1n$  or  $Pmnb$ . The crystal used to collect intensity data measured  $0.1 \times 0.6 \times 0.6 \text{ mm}$  and was mounted in a sealed Lindemann-glass capillary parallel to the  $c$ -axis. Integrated Weissenberg photographs were taken with filtered  $\text{CuK}\alpha$ -radiation using multiple film technique and equi-inclination geometry. Data were collected from zero through the fourth layer. A total of 379 independent reflections were explored of which 290 were measurable. The intensities were evaluated with a microphotometer and the different layers were placed on the same relative scale using PAILRED data. Corrections for Lorentz and polarization factors and spot size were made but no absorption correction was applied. The data were placed on an absolute scale and corrected for thermal motion in order to calculate  $E$ -values. The following statistical averages were obtained.

	$\langle  E  \rangle$	$\langle E^2 \rangle$	$\langle  E^2 - 1  \rangle$
Observed:	0.810	1.000	0.926
Theoretical for centric:	0.798	1.000	0.968
Theoretical for acentric:	0.886	1.000	0.736

The above statistics favour the centrosymmetrical space group but the possible symmetry of the molecule together with the requirement in the centrosymmetrical space group  $Pmnb$  that the four molecules in the unit cell must be either in special positions or in the eight general positions, led to the initial choice of the acentric group  $Pc2_1n$  with four molecules in general positions.

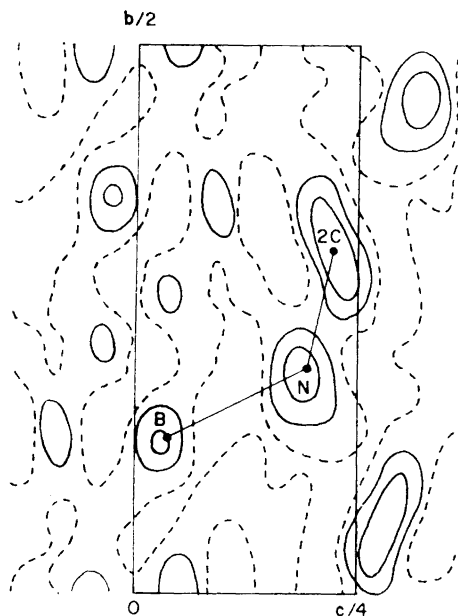


Fig. 1.  $E$ -map of the  $a$ -axis projection calculated from 18 signs determined by the symbolic addition procedure. The final positions of the non-hydrogen atoms are indicated.

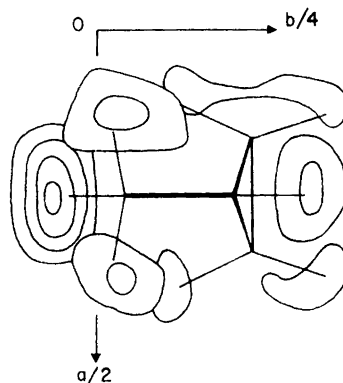


Fig. 2. Three-dimensional difference Fourier synthesis seen along the  $c$ -axis, showing approximate positions of hydrogen atoms. Contours are at equal arbitrary intervals.

## STRUCTURE DETERMINATION

A spherical, sharpened Patterson section, with origin removed, was calculated at a radius of 1.5 Å. It clearly indicated a three membered ring approximately in the (010) plane with the remaining non-hydrogen bond about 60° from that plane in the *c*-axis direction. A direct sign determination approach was adopted for the only centrosymmetric projection [100]. Although only 18 signs were determined, the resulting *E*-map (Fig. 1) clearly showed the molecular orientation in the cell. The first three dimensional structure factor calculation gave an *R*-value of 33 % for the observed reflections.

## REFINEMENT OF THE STRUCTURE

The refinement of the positional and thermal parameters was carried out using the full-matrix least squares IBM 7090 program written by Busing, Martin and Levy.<sup>2</sup> The scattering factors from the *International Tables for X-ray Crystallography* (p. 202)<sup>3</sup> were used. The first cycle of refinement, using unit weight and isotropic temperature factors, brought the *R*-value down to 16 % with only the contribution of the nitrogen, carbon, and boron atoms taken into account. Introduction of anisotropic temperature factors reduced the *R*-value to 12.5 %. At this stage a difference map was calculated which clearly showed the positions of the eight hydrogen atoms (Fig. 2). The only additional maximum, with a height of a hydrogen atom, was located in the middle of the carbon-carbon bond. The hydrogens were introduced at the positions indicated by the difference synthesis and were given the anisotropic factors of the corresponding "heavy" atoms. The weighted *R*-value  $[\sum(F_o - F_c)^2]^{1/2} / [\sum F_o^2]^{1/2}$ , with the hydrogen positions refined, went down to 5.7 %. During all these non-centrosymmetric calculations the *x*-coordinate of the central nitrogen atom had been fixed at 0.25. An examination of the boron and carbon positions showed that the deviation from their "centrosymmetric" positions was only 0.021 and 0.022 Å, respectively. As this was not significant the structure was finally refined in the centrosymmetrical spacegroup *Pmnb* with the boron and nitrogen atoms and two of the hydrogens in the mirror plane. This reduced the estimated standard deviations (e.s.d.) by a factor of 2 to 4. The final *R*-values with and without the nonobserved reflections were 10.8 and 8.7 %, respectively. All through the calculations the nonobserved reflections were given half the minimum observable intensities. The observed and calculated structure factors are given in Table 1, and the final positional and thermal parameters in Table 2.

## DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The structure analysis has clearly revealed the correct structural configuration as aziridine borane, according to formula I. The mirror symmetry of the molecule is utilized in the crystal structure with the nitrogen and boron atoms in the mirror planes at *x* equal to 1/4 and 3/4. All the intramolecular

Table 1. Observed and calculated structure factors  $\times 10$ . \* indicates nonobserved reflections.

Table with 12 columns representing h, k, l, F\_o, F\_c and their respective values for various reflections. The data is organized in four groups of three columns each, with some cells containing asterisks to indicate nonobserved reflections.

Table 2. Positional and vibrational parameters  $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{21} + 2hl\beta_{31} + 2kl\beta_{23})]$  of the atoms times  $10^4$  for the "heavy" atoms and times  $10^3$  for the hydrogens. E.s.d. are given for each parameter.

Table with 10 columns: Atom, x, y, z, \beta\_{11}, \beta\_{22}, \beta\_{33}, \beta\_{12}, \beta\_{13}, \beta\_{23}. It lists parameters for N, C, B, and five H atoms with associated error values.

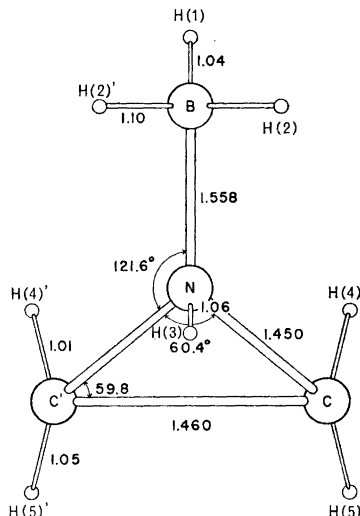


Fig. 3. Diagram showing bond distances for all atoms and angles involving non-hydrogen atoms.

bond distances and angles are given in Table 3 and partly in Fig. 3. The B—N bond length is in good agreement with those found in addition compounds.<sup>4</sup> In the aziridine ring the C—N bond length seems to agree well with a single C—N bond whereas the C—C bond of 1.460 Å is remarkably short. Turner, Fiora and Kendrick<sup>5</sup> have given some structural parameters of ethyleneimine (aziridine) from microwave studies.

	Turner <i>et al.</i> <sup>5</sup>	This work
C—C	1.480 Å	1.460 ( $\pm 9$ ) Å
C—N	1.488	1.450 ( $\pm 6$ )
C—H	1.083	1.01 and 1.05 ( $\pm 4$ )
$\angle$ HCH	116°41'	135 $\pm$ 3°

Table 3. Distances and angles. The symmetry operation indicated by ' is  $(1/2-x; y; z)$  and by ''  $(x; 1/2+y; 1/2-z)$ .

B —N	1.558 $\pm$ 6 Å	B —N —C	121.6 $\pm$ 3°
C —N	1.450 $\pm$ 6	C —N —C'	60.4 $\pm$ 4
C —C'	1.460 $\pm$ 9	N —C —C'	59.8 $\pm$ 2
B —H(1)	1.04 $\pm$ 6	N —B —H(1)	103 $\pm$ 3
B —H(2)	1.10 $\pm$ 4	N —B —H(2)	113 $\pm$ 2
N —H(3)	1.06 $\pm$ 6	H(1)—B —H(2)	115 $\pm$ 3
C —H(4)	1.01 $\pm$ 4	H(2)—B —H(2)'	97 $\pm$ 4
C —H(5)	1.05 $\pm$ 4	C —N —H(3)	111 $\pm$ 2
B —H(4)	2.26 $\pm$ 4	B —N —H(3)	118 $\pm$ 3
N —B''	3.288 $\pm$ 7	N —C —H(4)	88 $\pm$ 3
H(3)—B''	2.29 $\pm$ 5	N —C —H(5)	128 $\pm$ 3
		C' —C —H(4)	115 $\pm$ 3
		C' —C —H(5)	107 $\pm$ 2
		H(4)—C —H(5)	135 $\pm$ 3
		N —H(3)—B''	157 $\pm$ 4

The angle between the CC'N plane and N—H(3) was found to be  $112^\circ$  which is very close to  $115 \pm 3^\circ$  found in this work. The calculations by Turner *et al.* assumed an N—H distance of 1.000 Å. Though no e.s.d. are given, the conclusion might be drawn that the addition of  $\text{BH}_3$  to the nitrogen introduces a shortening of the C—N bonds in the aziridine ring. The distances from carbon and nitrogen to their respective hydrogens seem normal and so are the B—H bonds.<sup>6</sup> The only intermolecular distance that does not agree with accepted van der Waals' distances is that between boron and nitrogen in neighbouring molecules along the *b*-axis as seen in Fig. 4. The distances

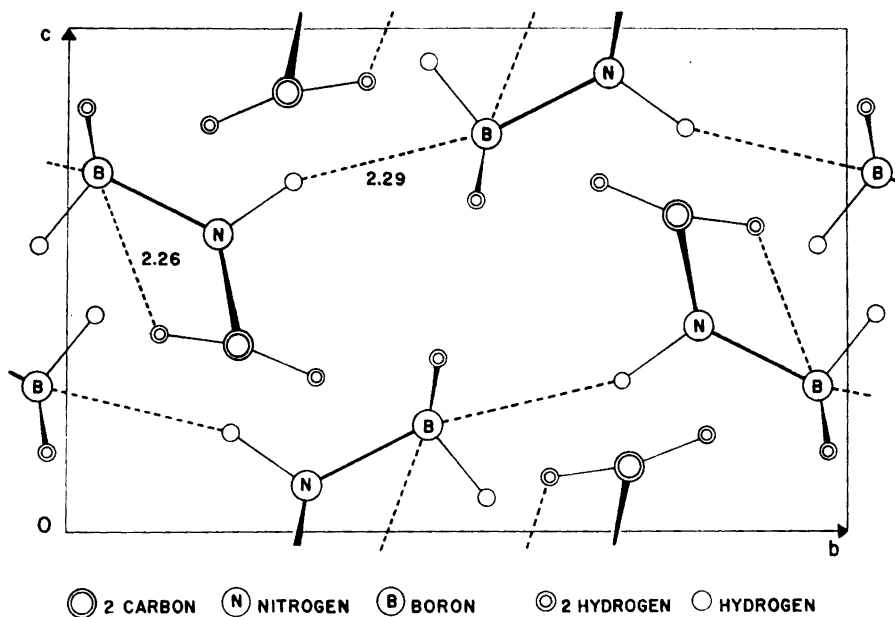


Fig. 4. Drawing of the crystal structure projected along the *a*-axis.

Table 4. The r.m.s. components of thermal displacement of the atoms along the ellipsoid axes ( $\times 10^3$  Å) and the angle between these axes and the crystallographic axes in degrees.

Atom		<i>a</i>	<i>b</i>	<i>c</i>
N	$171 \pm 5$	90	$177 \pm 2$	$87 \pm 2$
	$238 \pm 5$	0	90	90
	$266 \pm 6$	90	$87 \pm 2$	$3 \pm 2$
C	$216 \pm 5$	$81 \pm 3$	$159 \pm 2$	$72 \pm 2$
	$296 \pm 5$	$28 \pm 3$	$74 \pm 3$	$68 \pm 3$
	$371 \pm 6$	$116 \pm 3$	$78 \pm 2$	$29 \pm 3$
B	$184 \pm 6$	90	$174 \pm 3$	$84 \pm 3$
	$284 \pm 10$	90	$96 \pm 3$	$174 \pm 3$
	$298 \pm 7$	0	90	90

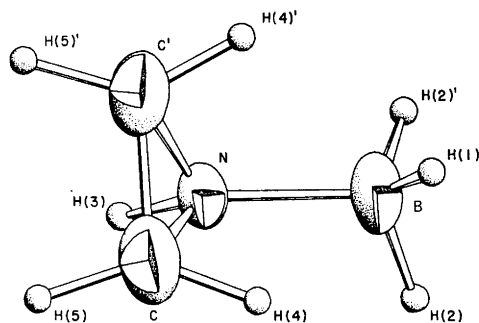


Fig. 5. Thermal ellipsoid representation of an aziridine borane molecule. Ellipsoids enclose 30 % probability. Structure viewed along an axis 15 degrees from the crystallographic *c*-axis.

involved are given in Table 3. The  $N(H)\cdots B''$  distance, corrected for independent thermal motion, of 3.332 (7) Å probably indicates a weak charge-transfer bond. The corresponding  $H(3)\cdots B''$  distance of 2.29 Å is comparable with the intramolecular distance  $H(4)\cdots B$  of 2.26 Å, as shown in Fig. 4.

The anisotropy of the temperature motion of the "heavy" atoms is tabulated in Table 4 and shown in Fig. 5 where the ellipsoids are drawn with 30 % probability.

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