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A Reinvestigation of the Crystal and Molecular Structure of Hexachloroborazine

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The intra- and intermolecular electrostatic interactions in hexachloroborazine are discussed, and are combined with CNDO/BW semi-empirical molecular-orbital calculations, and with the results of similar calculations on borazine and *B*-trichloroborazine to show that hexachloroborazine has a regular hexagonal ring structure. The X-ray diffraction analysis of Haasnoot, Verschoor, Romers & Groeneveld [*Acta Cryst.* (1972). B**28**, 2070–2073] indicated alternating B–N bond lengths. The X-ray diffraction data have been reinterpreted and shown to be consistent with a regular hexagonal ring structure for hexachloroborazine.

Introduction

The interpretation of a recent X-ray diffraction study of hexachloroborazine (HCB) by Haasnoot, Verschoor, Romers & Groeneveld (1972) indicated a borazine ring structure with alternating bond lengths, 1·398 and 1·451 Å. This differs from borazine and *B*-trichloroborazine (TCB), each of which contains a planar conjugated ring of equal B–N bond lengths, and suggested to us that calculations should be performed to see whether the alternation of B–N bond lengths in HCB could be explained theoretically. Such bond alternation could either occur in the free molecule, or be due to distortion of the symmetric free molecule in the crystal lattice. In the free molecule the possible alternation of bond lengths due to electrostatic interactions between charged atoms was studied classically. Then borazine, TCB and HCB were studied as free molecules with the CNDO/BW theory (Boyd & Whitehead, 1972) to see whether any bond alternation occurred in HCB due to energy dependence on charge separation in the molecule. Finally the CNDO/BW charges for HCB were used to calculate the classical electrostatic interactions between the atoms in a central molecule and all the atoms in the 12 nearest neighbouring molecules in the crystal lattice, to see whether this resulted in alternating B–N bond lengths.

Since all the theoretical calculations suggested equal B–N bond lengths in HCB, the X-ray diffraction data, kindly made available to us by J. G. Haasnoot, have been re-examined. With computer programs for the investigation of twinned, disordered and pseudo-symmetric crystal structures, it has been shown that the minimization function has two minima: one corresponds to the structure of Haasnoot *et al.* (1972), and the other, extremely close to the first, is slightly deeper and corresponds to a regular molecular structure.

Theory

(*a*) *Intramolecular electrostatic interactions*

π-Electron (Roothaan & Mulliken, 1948; Davies, 1960; Chalvet, Daudel & Kaufman, 1965; Hansen & Messer, 1967), all-valence-electron (Hoffmann, 1964; Kuznesof & Shriver, 1968; Scherr & Haworth, 1973), and *ab initio* SCF MO calculations (Peyerimhoff & Buenker, 1970; Armstrong & Clark, 1972) on borazine have shown that the π-electron shift is from nitrogen towards boron, whereas the σ-electron shift is in the opposite direction. The net polarity of the atoms is B^+N^-. However, the magnitude of the predicted atomic charges varies widely: in Table 1 typical earlier values are compared with the present CNDO/BW results (see below).

The reported B–N bond-length alternation in the borazine ring could arise from the electrostatic attraction between the positively charged boron and the negatively charged nitrogen atoms, tending to move the atoms as indicated in Fig. 1. In this figure θ is the angle through which the triangle formed by the boron atoms is rotated about the triangle formed by the nitrogen atoms. $\theta=60°$ corresponds to the structure with equal B–N bond lengths; the structure with short (1·398 Å) and long (1·451 Å) bond lengths, proposed by Haasnoot *et al.* (1972), corresponds to $\theta=58·5°$.

If the atoms are assumed to be point charges, the electrostatic interaction energy, E, can be expressed in terms of the net atomic charges on boron (Q_B) and nitrogen (Q_N), the radius, r, of the circle which corresponds to the average B–N bond length (Fig. 1) and the angle of rotation, θ; *i.e.*

$$E=(3Q_BQ_N/r)[\sqrt{2}(1-\cos\theta)^{-1/2}+(2+\cos\theta-\sqrt{3}\sin\theta)^{-1/2}+(2+\cos\theta+\sqrt{3}\sin\theta)^{-1/2}]$$
$$=(3Q_BQ_N/r)f(\theta).$$

If the atomic charges are assumed not to vary with the B–N distance, E is proportional to $f(\theta)$. A plot of

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$-f(\theta)$ *vs.* θ is shown in Fig. 2. This plot shows no minimum for $60° > \theta > 0°$, and predicts the structure with equal bond lengths to be the least stable. Such an electrostatic treatment would not be expected to be valid outside a *very small range* in θ. Nevertheless this set of Coulomb attractive forces would be expected to lead to unequal bond lengths, as indeed it does. The actual bond lengths would then be the result of the minimization of the total energy due to these electrostatic forces, and the attractive and repulsive forces due to chemical bonding.

It is also necessary to consider the effect of chlorine substitution on the borazine ring structure. The procedure can be easily extended to the case of hexachloroborazine by including the chlorine atoms as point charges in the model represented by Fig. 1 and calculating the total electrostatic interaction energy as a function of θ. For these calculations, the ring structure corresponding to $\theta = 60°$ was taken to be a regular hexagon, with a B–N length of 1·425, and all bond angles equal to 120°. B–Cl and N–Cl distances used were 1·724 and 1·749 Å. The atomic charges Q_B, Q_N and Q_{Cl} were obtained from our CNDO/BW calculations on HCB (Table 1.) The resulting total electrostatic interaction energy is plotted as a function of θ in Fig. 3. The results are similar to those in Fig. 2 except for a small maximum of the energy around $\theta = 56·0°$, showing that purely electrostatic considerations do not favour the reported ring structure of HCB.

The total energy of the molecule, including electronic energy and nuclear repulsions, has, therefore, to be studied as a function of the B–N length, to see if the structure with alternating bond lengths is more stable than the one with equal bond lengths.

(*b*) *CNDO/BW molecular-orbital calculations*

Previous molecular-orbital calculations on borazine and substituted borazines including both σ- and π-electrons (Hoffmann, 1964; Kuznesof & Shriver, 1968; Scherr & Haworth, 1973) were concerned with the

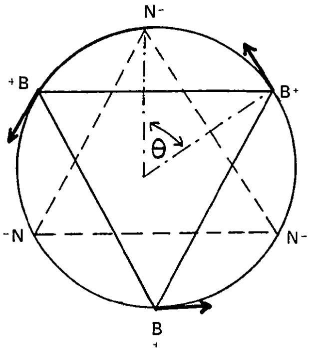

Fig. 1. Electrostatic model for B–N length alternation in the borazine ring.

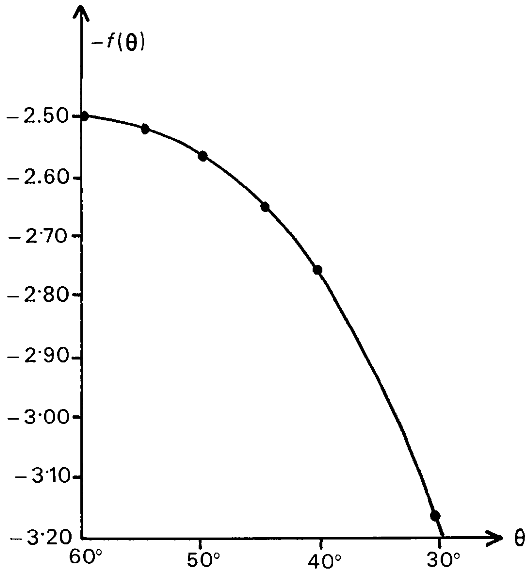

Fig. 2. Variation of electrostatic interaction in borazine as a function of angle θ defined in Fig. 1.

Table 1. *Charge distribution in borazine, trichloroborazine (TCB) and hexachloroborazine (HCB) calculated by several theoretical approaches*

Compound	Method	B	N	H(B)	H(N)	Cl(B)	Cl(N)	Reference
Borazine	EHT	0·938	−1·075	−0·162	0·299			1
	CNDO/1	0·322	−0·231	−0·160	0·069			2
	MWH	0·112	−0·145	−0·055	0·088			3
	ab initio	0·474	−0·735	−0·037	0·299			4
	CNDO/BW	0·567	−0·577	−0·149	0·159			5
TCB	MWH	0·177	−0·183		0·078	−0·072		3
	CNDO/BW	0·626	−0·643		0·169	−0·152		5
HCB	MWH	0·196	−0·120			−0·063	−0·013	3
	CNDO/BW	0·480	−0·240			−0·090	−0·150	5

References

(1) Extended Hückel theory: Hoffmann (1964).
(2) Complete neglect of differential overlap with theoretical evaluation from Slater orbitals of the electron repulsion and electron nuclear-attraction integrals: Kuznesof *et al.* (1968).
(3) Extended Hückel theory using the Mulliken–Wolfsberg–Helmholtz approximation for β: Scherr *et al.* (1973).
(4) Using a limited Gaussian-orbital basis set: Armstrong *et al.* (1972).
(5) This paper.

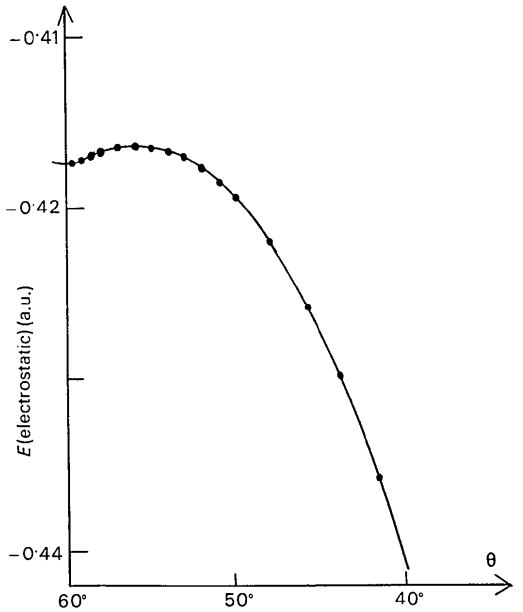

Fig. 3. Variation of electrostatic interaction in hexachloroborazine as a function of angle θ.

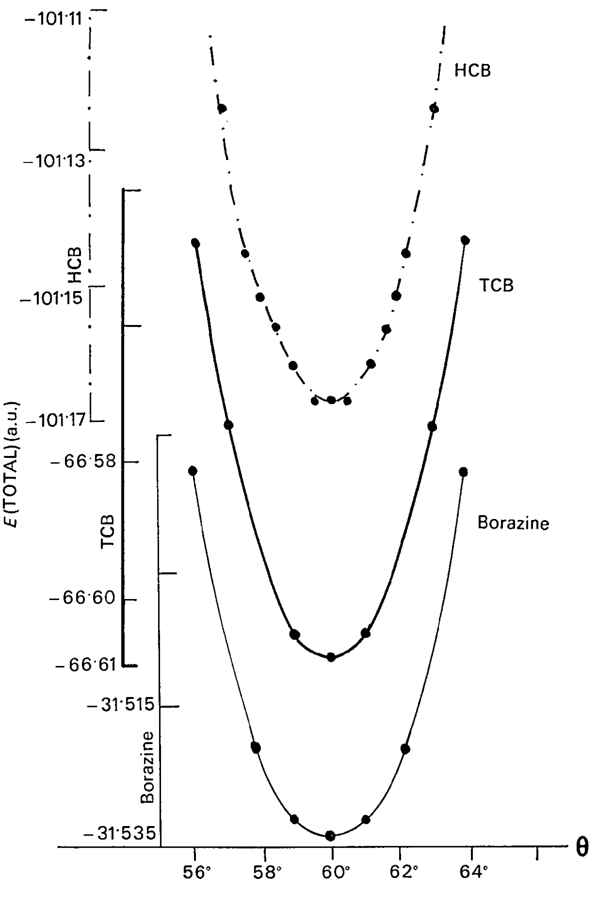

Fig. 4. Dependence of total energy on θ in borazine, *B*-trichloroborazine and hexachloroborazine. Results of CNDO/BW molecular-orbital calculations.

charge distribution and electronic spectra of these molecules. Armstrong & Clark (1972) have shown, from *ab initio* SCF MO calculations, that a planar D_{3h} structure for borazine is more stable than a non-planar twist-boat structure of C_2 symmetry, both of which fit the electron diffraction results for borazine (Harshbarger, Lee, Porter & Bauer, 1969). However, the question of the relative stability of planar structures with equal and alternating B–N lengths has not previously been studied. Such a study on borazine, TCB and HCB has now been performed with the semi-empirical CNDO/BW theory (Boyd & Whitehead, 1972). This method is particularly suitable for the present study since it is parameterized on diatomic and triatomic molecules to give the correct bond lengths and energy of a molecule. The core integrals, $U_{\mu\mu}$, and the one-centre electron repulsion integrals γ_{AA}, were taken from Sichel & Whitehead (1967). The two-centre electron repulsions were evaluated from the Ohno (1964) expression,

$$\gamma_{AB}=(R_{AB}^2+a^2)^{-1/2};\quad a=2/(\gamma_{AA}^*+\gamma_{BB}^*)\,.$$

The resonance integrals were evaluated by

$$H_{kl}=-\beta_{AB}S_{kl}\,.$$

Values for the bonding parameter, β_{AB}, and the core repulsion parameter, α, were taken from Set III of Tables 5 and 6 of Boyd & Whitehead (part I, 1972), since this is the set yielding consistently satisfactory bonding energies and nuclear quadrupole resonance field gradients (Boyd & Whitehead, 1972; Cohen & Whitehead, 1972). The additional parameters required in the present calculations were taken from the thesis of Boyd (1971):

$$\beta_{BN}=8\cdot30,\quad \beta_{BCl}=9\cdot55,\quad \beta_{NCl}=10\cdot80$$
$$\alpha_{BN}=2\cdot00,\quad \alpha_{BCl}=1\cdot30,\quad \alpha_{NCl}=1\cdot336\,.$$

An orbital exponent of 1·0 was used for the hydrogen 1*s* orbital in calculations involving hydrogen, since the effect of varying the Z'_H through the range of values commonly used in semi-empirical calculations showed that better results were obtained for orbital energies and force constants in CNDO/BW when the value $Z'_H=1\cdot0$ was used (Boyd, 1971).

The dependence of the total energy of the molecule on the B–N bond lengths (or equivalently on the angle θ in Fig. 1) was calculated in borazine, TCB and HCB. The geometry of the symmetric structure with all B–N bond lengths equal ($\theta=60°$) was taken from the results of Haasnoot *et al.* (1972) by averaging the unequal B–N bond lengths: B–N = 1·425 Å, B–Cl = 1·724 Å, N–Cl = 1·749 Å, B–H = 1·258 Å and N–H = 1·050 Å. All bond angles were taken to be 120°. The calculated total energies, including electrostatic effects, for borazine, TCB and HCB are plotted as functions of the angle of rotation in Fig. 4. The structure with equal B–N lengths is seen to be the most stable for all three molecules, and the structure with alternating B–N lengths, which corresponds to $\theta=58\cdot5°$, is unstable

Table 2. *N.q.r. parameters for borazine, B-trichloroborazine and hexachloroborazine*

CNDO/BW results. Frequency in MHz and η in %.

Nuclei	Compound	Calculated parameters		
		e^2Qq	η	
^{11}B	Borazine	−0·557	89·17	
	TCB	0·406	65·45	
	HCB	−1·008	21·50	
		ν_+	η	
	Borazine	2·953	79·15	
	TCB	−3·377	90·17	
	HCB	−3·375	27·61	
		ν_-		
^{14}N	Borazine	1·720		
	TCB	−1·816		
	HCB	−2·806		
		ν_d		
	Borazine	1·233		
	TCB	−1·561		
	HCB	−0·569		
		e^2Qq	η	
^{35}Cl	TCB	−50·33	8·75	
		(−40·20)*	(29·6)*	
	HCB	−52·45	0·002	Cl(B)
		−69·75	32·32	Cl(N)

* Experimental values: Kaplansky & Whitehead (1970).

compared to that with equal bond lengths by 3·25, 5·63 and 6·26 kcal mol^{-1} for borazine, TCB and HCB respectively. The calculated atomic charges in these molecules are given in Table 1.

Information about the presence of any asymmetric field in the crystal can be obtained from nuclear quadrupole resonance studies. An attempted study of n.q.r. in HCB has not been successful (Haasnoot, 1973). We have calculated the n.q.r. parameters for ^{11}B, ^{14}N and ^{35}Cl nuclei in borazine, TCB and HCB from the CNDO/BW *p*-orbital populations (Sichel & Whitehead, 1968; Cohen & Whitehead, 1972). The results are given in Table 2. Even though the calculated values are not in good agreement with the available experimental data (compare e^2Qq and η values for TCB) owing to limitations in the validity of the CNDO/BW parameters in charged systems (Sichel & Whitehead, 1967; Boyd, 1973; Anno & Sakai, 1972), these values serve as an estimate of the range of frequencies to be expected. The calculations are for isolated molecules with equal bond-length geometry for the borazine ring.

(*c*) *Intermolecular electrostatic effect*

Since the calculations on an isolated molecule of HCB show that it has all B–N bond lengths equal, it is pertinent to consider whether electrostatic attractions and repulsions between charges on neighbouring molecules in the crystal can lead to a B–N bond-length alternation. The crystal structure of HCB has been reported by Haasnoot *et al.* (1972). The space group is *R*3 with $a = 8{\cdot}847$ (4) and $c = 10{\cdot}321$ (5) Å in the hexagonal reference system. In our calculations the 12 nearest-neighbouring molecules around a given HCB molecule were considered. The molecules were assumed to have a regular hexagonal ring structure with a B–N bond length of 1·425 Å. Boron, nitrogen and chlorine atoms were assumed to be point charges, the numerical values of these charges being given by our CNDO/BW results (Table 1). The magnitude of the resultant force and its components, arising from the electrostatic attractions and repulsions between boron, nitrogen and chlorine of the central molecule and the atomic charges on all atoms of the 12 neighbouring molecules, was computed (Fig. 5). The results are schematically shown in Fig. 6. It is interesting to note from this figure that the directions of the resultant forces on the boron and nitrogen atoms are such that they can lead to a B–N bond-length alternation. However the effectiveness of this intermolecular interaction force in altering the

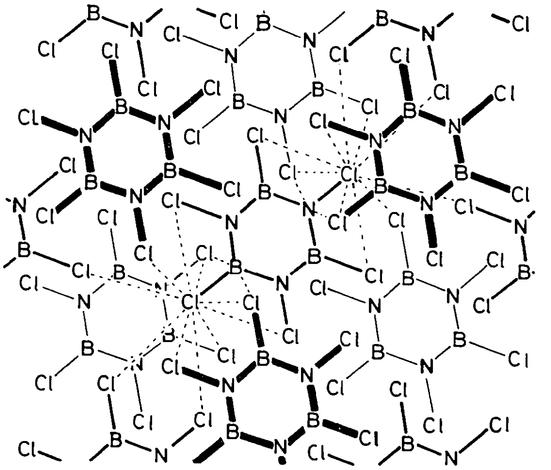

Fig. 5. The crystal structure of hexachloroborazine from refinement 4 of the present work, projected down **c**. Relative to the central molecule those bonds in heavy lines are in the next plane in the +**c** direction. Those in light lines are in the next plane in the −**c** direction. The chlorine attached to a nitrogen makes ten contacts shorter than 4 Å with other chlorine atoms: In plane of molecule: a contact of 3·162 Å and one of 3·165 Å to boron chlorines in the molecule; a contact of 3·618 Å to a boron chlorine and two contacts at 3·586 Å to nitrogen chlorines (related by a threefold symmetry axis) in other molecules. Next plane in +**c** direction: a contact at 3·915 Å to a nitrogen chlorine and a contact at 3·831 Å to a boron chlorine: Next plane in −**c** direction: a contact at 3·915 Å to a nitrogen, chlorine two contacts at 3·969 Å to boron chlorines (related by a threefold symmetry axis). The nitrogen atom is 3·613 Å from a boron chlorine in the next +**c** plane and 3·669 Å from a nitrogen chlorine in the −**c** direction. Similarly the chlorine atom attached to boron makes 10 contacts shorter than 4 Å with other chlorines: In plane of molecule: a contact of 3·162 Å and one of 3·165 Å to nitrogen chlorines in the molecule, a contact of 3·618 Å to a nitrogen chlorine and two contacts of 3·577 Å to boron chlorines (related by a threefold symmetry axis) in other molecules: Next plane in +**c** direction: a contact of 3·918 Å to a boron chlorine and two contacts at 3·969 Å to nitrogen chlorines (related by threefold symmetry axis): Next plane in −**c** direction: a contact at 3·918 Å to a boron chlorine and a contact at 3·831 Å to a nitrogen chlorine. The boron atom is 3·609 Å from a nitrogen chlorine in the next −**c** plane, and 3·665 Å from a boron chlorine in the +**c** direction.

B–N bond length can only be decided by a numerical estimate of the displacements that the boron and nitrogen atoms can undergo under the influence of these forces. An approximate estimate of this can be obtained from the relation

$$k\Delta r = F,$$

where k is the force constant of the B–N bond, F the calculated resultant electrostatic force and Δr is the maximum displacement of the atom from its equilibrium position. The average frequency of the B–N stretch vibration in borazines is around 1400 cm^{-1} (Niedenzu & Dawson, 1965), which corresponds to a force constant of $7{\cdot}14 \times 10^5$ dyn cm^{-1}. The calculated resultant forces on boron ($4{\cdot}9 \times 10^{-4}$ a.u.) and nitrogen ($9{\cdot}9 \times 10^{-3}$ a.u.) thus lead to a maximum displacement of 0·00057 Å for boron and 0·011 Å for nitrogen. Even these maximum displacements are too small to account for the reported bond-length change of 0·03 Å in HCB.

All present theoretical considerations thus lead to the conclusion that the B–N rings in borazine, TCB and HCB are similar and have a regular hexagonal structure. Interestingly, a normal coordinate analysis of the infrared spectrum of HCB (Haasnoot, 1973) also suggests a structure with equal B–N bond lengths. In view of these results, a re-examination of the X-ray diffraction results for HCB has been carried out. A bond-length dependent application of CNDO/BW and the use of a theoretical force constant in the interpretation of the crystal lattice electrostatic effects will be reported later.

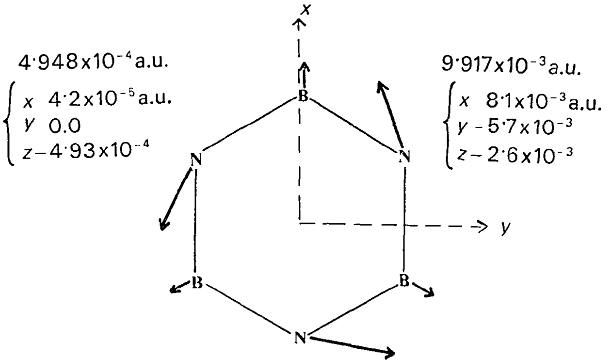

Fig. 6. Effect of intermolecular electrostatic forces in hexachloroborazine. The arrows indicate the direction of the resultant forces on the atoms. The figures give the magnitudes of the forces and the numbers in parentheses give their x, y and z components.

X-ray results

Details of the experimental results for HCB are given by Haasnoot *et al.* (1972). Structure amplitudes were obtained for 781 unique reflexions; $F(hkl)$ and $F(\bar{h}\bar{k}\bar{l})$ were considered independent. In the present calculations reflexions that were indicated as unobserved by Haasnoot *et al.* were not used, so that only 735 reflexions remained. Also, for some calculations, $F(hkl)$ and $F(\bar{h}\bar{k}\bar{l})$ were not considered as independent, but were averaged, to give a total of 430 unique reflexions.

Form factors for the neutral atoms were taken from Cromer & Mann (1967), apart from the real and imaginary components of the dispersion corrections, which were taken from *International Tables for X-ray Crystallography* (1962). The data available to us had been corrected for extinction effects by Haasnoot *et al.* (1973).

Table 3. *Summary of refinements*

Number	N position	Description	R	R_ω
1	1	Unmerged data, weighting scheme (*a*)	0·0254	0·0274
2	2	Unmerged data, weighting scheme (*a*)	0·0253	0·0271
3	2	Merged data, weighting scheme (*b*)	0·0209	0·0268
4	2	Unmerged data, weighting scheme (*a*) and a constrained model	0·0254	0·0272

Notes

(1) All the refinements refer to a fully anisotropic model, and apart from refinement 3, the imaginary part of the anomalous dispersion correction was included.

(2) $R=\sum(||F_o|-|F_c||)/\sum(|F_o|)$. $R_\omega=[\sum\omega(|F_o|-|F_c|)^2/\sum\omega|F_o|^2]^{1/2}$.

(3) Both weighting schemes were determined empirically at the end of a refinement based upon an anisotropic model and unit weights. The weights were computed from a Chebyshev polynomial, whose coefficients were estimated so that the root-mean-square value of $\omega(|F_o|-|F_c|)^2$ remained approximately constant for all groups of reflexions.

Weighting scheme (*a*) was determined during refinement number 1, and is given by:

$$\omega_a = 1/[365T_0^*(x) + 557T_1^*(x) + 237T_2^*(x) + 44T_3^*(x)],$$

where $x=|F_o|/|F_o|_{\max}$ and $T_i^*(x)$ are given by Rollett (1965).

Weighting scheme (*b*) was determined during refinement number 3, and is given by:

$$\omega_b = 1/[5{\cdot}9T_0^*(x) + 5{\cdot}8T_1^*(x) + 1{\cdot}4T_2^*(x) + 1{\cdot}8T_3^*(x) + 1{\cdot}5T_4^*(x)].$$

Table 4. *Differences found between various refinements*

	Positional parameters		Thermal parameters	
Refinements	Maximum (Å)	r.m.s. (Å)	Maximum (Å^2)	r.m.s. (Å^2)
Haasnoot *et al.* (1972) Refinement 1	0·012	0·007	0·0112	0·0037
Haasnoot *et al.* (1972) Refinement 2	0·028	0·021	0·0144	0·0067
Refinement 1 Refinement 2	0·032	0·023	0·0104	0·0049
Refinement 2 Refinement 4	0·007	0·003	0·0015	0·0004

(*a*) *Refinements*

The various refinements carried out are summarized in Table 3. For all the refinements the same course was followed: namely, isotropic refinement with unit weights, anisotropic refinement also with unit weights, and finally anisotropic refinement with a set of empirical weights. The parameters resulting from the various refinements are given in Table 5 and their differences are compared in Table 4.

Refinement number 1 started from the coordinates given by Haasnoot *et al.* (1972) for their model 6. From Table 4 it can be seen that the discrepancies between the present final coordinates and those of Haasnoot *et al.* are not large, and are probably caused by differences between the weighting schemes and form factors used in the two analyses. At the end of refinement number 1 the vibration of the B atom appeared to be much less than that of the N atom. For this reason, the B and N atoms were interchanged (column 2, Table 3: the N atom moves from position 1 to position 2). Such a change has a small effect on the structure, apart from simply replacing it by its enantiomorph.

Table 5. *Final atomic parameters*

All parameters are × 10^4.

Line 1: Parameters from model 6 of Haasnoot *et al.* (1972).
Line 2: Parameters from refinement 1 in Table 3.
Line 3: Parameters from refinement 2 in Table 3.
Line 4: Parameters from refinement 4 in Table 3.

	X/*a*	*Y*/*b*	*Z*/*c*
B(1)	1843	1217	−14
	1849 (5)	1224 (4)	−14 (6)
	1854 (4)	1198 (5)	−30 (6)
	1854 (5)	1205 (3)	−31 (6)
N(2)	−1822	−1168	−5
	−1810 (5)	−1154 (5)	−5 (6)
	−1807 (5)	−1184 (5)	−19 (6)
	−1808 (5)	−1176 (3)	−21 (6)
Cl(3)	4064	2642	−51
	4068 (2)	2647 (3)	−51 (1)
	4069 (2)	2657 (2)	−52 (1)
	4069 (2)	2657 (2)	−52 (1)
Cl(4)	−4063	−2667	0
	−4063 (1)	−2664 (3)	0
	−4062 (1)	−2654 (3)	0
	−4062 (1)	−2654 (3)	0

However, the results of refinement number 2 reveal a second minimum in the minimization function, at a maximum distance of 0·03 Å for the light atoms, and of 0·01 Å for the chlorine atoms, from the minimum of refinement 1. In fact, the ratio of the weighted *R* values is 1·010, whereas there is a probability of 0·005 that the ratio will exceed 1·006, even if the higher value corresponds to one less degree of freedom (Hamilton, 1965). Hence the original structure can be excluded with a very low possibility of error. The new model resulting from refinement 2 differs only slightly from that of refinement 1, mainly in the *z* coordinates. However, these small changes are sufficient to lead to a much more symmetrical molecule, although the B–N bonds are still not equal.

Only the chlorine atoms, which form an approximately centrosymmetric array, have a significant imaginary component of the form factor for Mo *Kα* radiation. Consequently, refinement 2 was repeated with the merged data, generating the results for refinement 3. Hamilton's test is not strictly applicable to the ratio of these weighted *R* values, which give no clear indication in favour of the use of merged data. Therefore no further use of merged data was made. Refinement 2 gave the two B–N distances as 1·436 and 1·412 Å. A single constraint, that the distance should be equal to the mean value, with a standard deviation of 0·005 Å was applied. [The constraint was applied as an extra observational equation, in the way first suggested by Waser (1963) and discussed by Rollett (1970).] The ratio between the resulting weighted *R* values and that for the unconstrained model is 1·002. The probability of exceeding the ratio of 1·002 is 0·100, so that the constrained model cannot be excluded without appreciable risk.

(*b*) *Discussion of the false minimum problem*

The structure found differs from that of Haasnoot *et al.* by very small shifts of the atomic positions. This is somewhat disturbing because it undermines the confidence which can be placed in the results of a crystal-structure analysis, even when the agreement between the observed and calculated amplitudes is exception-

Table 5 (*cont.*)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
B(1)	366	207	462	19	−44	106
	254 (17)	193 (14)	454 (27)	19 (12)	7 (17)	73 (11)
	222 (17)	280 (19)	467 (26)	9 (15)	18 (17)	136 (14)
	229 (17)	267 (19)	471 (26)	8 (15)	15 (18)	130 (15)
N(2)	308	254	507	−8	38	214
	394 (19)	536 (21)	499 (27)	−24 (15)	−1 (18)	243 (15)
	427 (21)	433 (23)	491 (24)	2 (14)	−5 (19)	164 (17)
	417 (20)	448 (23)	488 (23)	1 (14)	−1 (19)	168 (17)
Cl(3)	366	416	851	−16	22	151
	381 (8)	420 (6)	814 (14)	−14 (6)	−8 (6)	181 (5)
	398 (8)	436 (7)	710 (9)	−14 (6)	−7 (5)	193 (6)
	399 (9)	435 (7)	709 (9)	−13 (6)	−8 (5)	191 (6)
Cl(4)	345	478	723	27	10	140
	321 (7)	473 (9)	744 (12)	21 (6)	40 (6)	102 (6)
	301 (7)	461 (9)	860 (12)	23 (6)	41 (6)	89 (6)
	300 (7)	461 (9)	862 (12)	23 (7)	42 (6)	91 (6)

ally good. The difficulty arises, in this case, because the structure deviates from a situation of higher symmetry by small shifts. Some warning of the difficulty is given by the full-matrix least-squares refinement. This converges with increasing slowness as the parameters approach those for either minima. Such a departure from the usual behaviour of the full-matrix least-squares process is a sure indication that the minimization function is not approximately quadratic in the parameter values. The direction in which the other minimum lies, when we have reached one minimum, can also be found. At each minimum, the normal matrix has one very small latent root (three times smaller than any other in this case). The latent vector corresponding to this latent root has elements which nearly all agree in sign with the differences between the parameter values for the two minima. This vector defines the direction in parameter space for which the curvature of the minimization function is least. It is not surprising that this direction is close to that leading to the other minimum.

(*c*) *Discussion of the molecular geometry*

The final model is that of refinement 4 in Table 3. The distances and angles for this model are given in Table 6. The two independent B–N distances differ only by 0·002 Å, because of the use of an inexact constraint in the refinement. This difference is smaller than the standard deviation for the constraint and has no significance.

Table 6. *Distances* (Å) *and angles* (°) *based on the parameters from refinement* 4

	Value	Mean
B(1)—N(2′)	1·425 (2)	
B(1)—N(2″)	1·423 (3)	1·424 (1)
B(1)—Cl(3)	1·724 (4)	1·724 (4)
N(2)—Cl(4)	1·755 (4)	1·755 (4)
N(2′)–B(1)–N(2″)	117·5 (5)	117·5 (5)
N(2′)–B(1)–Cl(3)	121·6 (5)	
N(2″)–B(1)–Cl(3)	120·9 (5)	121·3 (3)
B(1′)–N(2)–B(1″)	122·5 (5)	122·5 (5)
B(1′)–N(2)–Cl(4)	119·1 (5)	
B(1″)–N(2)–Cl(4)	118·4 (5)	118·8 (3)

The two B–N–Cl angles differ by 0·7° and the two N–B–Cl angles also differ by 0·7°. Again these differences are small in relation to their standard deviations, so that over all we have no evidence for departure of the molecule from $3m$ symmetry. The intramolecular distances and angles for such a model are also given in Table 6 as the mean values. The structure is shown in Fig. 5.

Conclusion

Both a re-examination of the X-ray data on hexachloroborazine and a semi-empirical molecular-orbital treatment of the structure of hexachloroborazine suggest that the borazine ring has equal B–N bond lengths of 1·424 (1) Å.

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