On the Crystal and Molecular Structure of Hexachloroborazine

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Crystals of hexachloroborazine, obtained by crystallization from tetrachloromethane, are rhombohedral. The space group is $R3$, $a = 6\cdot158$ Å, $\alpha = 91\cdot83°$ and $Z = 1$. The structure was solved by Patterson methods and refined with the least-squares technique using diffractometer data recorded with Mo $K\alpha$ radiation. The molecular symmetry is C_3, the short and long B–N bond lengths are $1\cdot398$ and $1\cdot451$ Å, the B–Cl and N–Cl bond lengths are $1\cdot724$ and $1\cdot749$ Å.

Introduction

This study forms part of a research project on *N*-chloro boron–nitrogen compounds. The aim of the present investigation was to verify the expected ring structure and its geometry in order to perform a normal coordinate analysis, which will be described elsewhere (Haasnoot & Groeneveld, 1972).

During the preparation of this paper the crystal structure of hexachloroborazine was described in this journal (Müller, 1971). Although our results and Müller's agree essentially there are a number of differences which justify an additional description. Müller's determination is based on 164 photographically recorded reflexions, obtained with a twinned crystal using Cu $K\alpha$ radiation; ours, obtained with an untwinned crystal, is based upon 754 reflexions, recorded with a diffractometer using Mo $K\alpha$ radiation. Since we paid utmost attention to correcting for absorption and secondary extinction, we feel that our results are more accurate, enabling us to give a verdict on the correct space group and molecular symmetry.

Experimental

Hexachloroborazine (HCB) was prepared by the reaction of nitrogen trichloride and boron trichloride in tetrachloromethane according to the procedure described by Haasnoot & Groeneveld (1967). The crystals obtained by sublimation are hexagonal, prismatic needles; those obtained by crystallization from the reaction mixture in tetrachloromethane have a rhombohedral, nearly cubic habit. The crystals with the hexagonal habit are invariably twinned rhombohedral specimens with (111) as the twinning plane (Müller, 1971). Crystals with the rhombohedral habit were used in the diffraction experiments discussed in this paper.

The unit-cell parameters were determined with a three-circle diffractometer. The lattice constants together with other crystal data are listed in Table 1.

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The intensities of 1800 reflexions up to $\theta = 30°$ were recorded with the automatic diffractometer, employing the θ–2θ scan. The procedures for the measurement and the assignment of the weights to the reflexion intensities have been described elsewhere (Verschoor & Keulen, 1971; Portheine, Romers & Rutten, 1972). The crystal with dimensions $0\cdot35 \times 0\cdot48 \times 0\cdot50$ mm was mounted about $\mathbf{c}^*$.

Table 1. *Crystallographic data for* HCB

Hexachloroborazine: $B_3N_3Cl_6$
Melting point 187°C; space group $R3$
Rhombohedral system: $a = 6\cdot158 \pm 0\cdot003$ Å, $\alpha = 91\cdot83 \pm 0\cdot008°$.
Hexagonal system: $a = 8\cdot847 \pm 0\cdot004$, $c = 10\cdot321 \pm 0\cdot005$ Å, at 20°C.
$d_o^{20} = 1\cdot96$ g.cm^{-3} (pycnometer method), $d_x^{20} = 2\cdot04$ g.cm^{-3}.
V(rhombohedral) $= 233\cdot2$ Å^3, $Z = 1$; μ (Mo $K\alpha$) $= 17\cdot63$ cm^{-1}.
$(hkl)_{hex} = (1\bar{1}0/01\bar{1}/111)$ $(hkl)_{rhomb}$.

On account of the large linear absorption coefficient (see Table 1) we used Mo Kα radiation ($\lambda = 0\cdot71069$ Å) filtered by zirconium. 50 reflexions had intensities smaller than twice the standard deviations found from counting statistics. These reflexions were considered to be unobserved.

By means of a correction method developed in this laboratory by de Graaff (1972) we calculated for each reflexion the transmission factor to a precision of 1%. The values of the transmission factor varied between $0\cdot39$ and $0\cdot51$. After dividing the recorded intensities by the appropriate transmission factors, the differences between equivalent reflexions were reduced from 15% to less than 3%.

Finally we calculated weighted mean values of equivalent reflexions. The intensities were now divided by the Lorentz and polarization factors and reduced to 781 independent structure factors, including 27 unobserved ones.

Structure determination

Since a hexagonal description can be visualized much better than a rhombohedral one, we switched to the hexagonal reference system. The structure was refined

Table 2. *Summary of applied refinement procedures*

$R = \sum ||F_o| - |F_c||/\sum|F_o|$, $R_w = \sum w(|F_o| - |F_c|)^2/\sum wF_o^2$

| Cycle (model)	Description	R	R_w
1	Starting model	15·0	
2	Anisotropic temperature parameters	6·2	
3	Assignment of weights σ^{-2}	3·92	4·33
4	Anomalous scattering	3·90	4·31
5	Omission of 15 strongest reflexions	2·73	3·48
6	Extinction correction on all reflexions	2·69	3·34
7	Including non-observed reflexions	2·80	
8	Cycle 6 with model (a) (Fig. 1)	2·95	4·27
9	Cycle 6 with model (b) (Fig. 1)	2·52	3·33
10	Cycle 6 with bond lenghts constraints	2·80	3·53

CHLORINE ◯
NITROGEN o
CARBON ●
BORON ✕
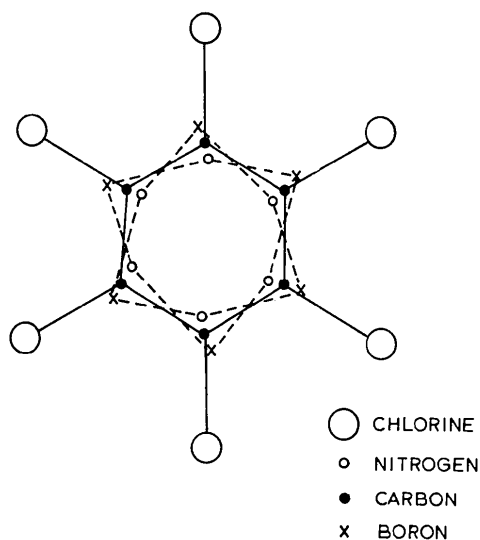
Fig. 1. Disordered arrangements of molecules of HCB. (a) ————model with symmetry $\bar{3}$ having carbon atoms in the ring. (b) – – – – disordered half molecules with symmetry 3. The differences between the models are exaggerated in the drawing.
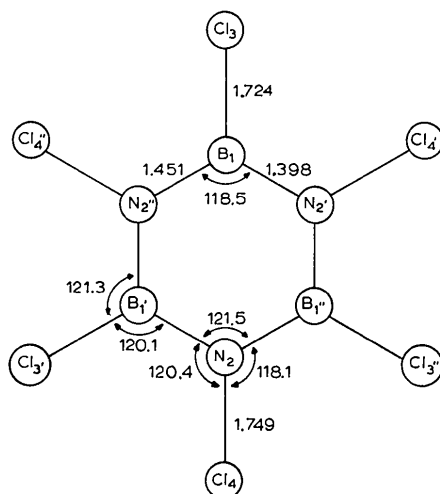

Fig. 2. Bond lengths (Å) and valency angles (°) in HCB.

with the least-squares method using the full-matrix version. Table 2 gives a summary of the applied procedures.

It can be seen that the refinement including anomalous scattering only produces a minor effect. This is hardly surprising since the chlorine atoms, on which the dispersion depends, constitute a nearly centrosymmetric configuration. The inverse structure gave identical results, obviously for the same reason.

Omission of the 15 strongest reflexions showed that extinction is important. Therefore, we applied a correction for secondary extinction according to the method proposed by Zachariasen (1969).

During the final stages of refinement we considered two disordered structures composed of molecules which are statistically distributed about two orientations differing by a rotation of 60° about the threefold axis. In the case of a 1:1 mixture the structures are conveniently described by the space group $R\bar{3}$. The two considered models (Fig. 1) are:

(a) 1:1 disordered model with symmetry $\bar{3}$ (S_6) approaching the symmetry $\bar{6}m2$ (D_{3h}).
The scattering factors of the light atoms are represented by those of carbon.

(b) A 1:1 mixture of two molecules each having occupation number 0·5, and each retaining the symmetry (C_3) as found in cycle 6.

Finally, during cycle 10 we returned to an ordered structure with space group $R3$, but constrained the molecule so as to possess equal bond lengths B–N and equal intramolecular Cl–Cl bonds. Introduction of the complete molecular symmetry $3m$ (C_{3v}), implying the relation:

$$U_{12} = (x^2 - y^2)^{-1}[(xy - \tfrac{1}{2}y^2)U_{11} - (xy - \tfrac{1}{2}x^2)U_{22}]$$

was, however, not possible with our programs.

Discussion of the molecular geometry

The positional and vibrational parameters of models resulting from cycles 6 and 10 are listed in Tables 3 and 4. A list of structure factors, based upon cycle 6, is available upon request.

Table 3. *The positional parameters (fractions of cell edges) and estimated standard deviations (10^4 Å) for HCB*

Upper line: model 6; lower line: model 10.

	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$
B(1)	0·1843	5	0·1217	4	−0·0014	5
	0·1831	4	0·1190	3	−0·0017	6
N(2)	−0·1822	5	−0·1168	4	−0·0005	5
	−0·1839	4	−0·1196	3	−0·0008	6
Cl(3)	0·4064	1	0·2642	2	−0·0051	1
	0·4059	1	0·2650	1	−0·0050	1
Cl(4)	−0·4063	1	−0·2667	2	0·0	
	−0·4069	1	−0·2657	1	0·0	

The alternative models 8 and 10 were inspected with Hamilton's (1965) R_w ratio test, assuming model 6 to be a zero hypothesis. It can be seen (Table 5) that models 8 and 10 must be rejected on a 0·5% significance level, if we assume that the distribution of errors is random. Accepting as a zero hypothesis, however, the centric disordered structure 9, model 6 cannot be rejected on the same significance level.

There is no compelling reason (on statistical grounds) to assume that disorder (in the sense of model 8 or 9) is present in the structure. Moreover the standard deviations of model 9 exceed those of model 6 by at least a factor of three.

Statistical and crystallographic arguments, therefore, favour to a high degree the acentric model derived from cycle 6 with unequal bond lengths B–Cl and N–Cl (Table 6, Fig. 2). This result is, perhaps, somewhat surprising. On theoretical grounds (valence bond structures, comparison with isoelectronic C_6Cl_6) one would expect equal B–N distances. The geometry of model 10 is included in Table 6.

Accepting model 6 as the correct structure we notice (Table 3) only minor differences between the z parameters of the four independent atoms. The endocyclic torsional angles are 1·2°, i.e. twice the standard deviation. We thus conclude that the ring is planar within the limits of accuracy. The exocyclic bonds are not exactly parallel to the plane of the ring: Cl(3) is 0·04 Å below and Cl(4) 0·01 Å above the plane of ring atoms. The puckered configuration of the chlorine atoms might very well be effected by mutual steric influence. The most important effect is that between two neighbouring chlorine atoms in the same molecule; the distance is 3·181 Å opposite a short B–N bond and 3·142 Å opposite a long B–N bond, the van der Waals diameter of a chlorine atom being 3·60 Å.

It can be seen (Table 7) that, in contrast with our observation, Müller finds a larger B–Cl distance and a smaller N–Cl distance. This discrepancy may be correlated with an interchange of B and N in the structure.

In their study of the structure of tetra-B-isocyanato-tetra-N-butylborazocine, Clarke & Powell (1966) also found an alternating boron–nitrogen ring system with distances very close to ours (Table 7). Following their

interpretation, HCB would be a triene system. This explanation might be acceptable for the borazocine ring characterized by the tub conformation, but seems rather unusual for the planar borazine ring. Hess (1969) found for the four membered diazadiboretidine alternating distances also, but he regarded the difference as insignificant in view of the standard deviations obtained. In Table 7 are listed geometrical entities of boron/nitrogen compounds relevant to this investigation. It can be seen that the results obtained for HCB strongly favour a ring structure with alternating B–N distances.

Table 5. *Numerical data for R_w ratio tests*

The symbols are explained in Hamilton (1964), significance level $\alpha = 0.005$.

	Model 6	Model 8	Model 9	Model 10
R	2·69	2·95	2·52	2·80
R_w	3·34	4·27	3·33	3·53
n	754	754	754	754
m	36	19	37	34
b	0(1)	17	0	2

$R_w(8)/R_w(6) = 1.279$ $R_w(10)/R_w(6) = 1.057$
$R(b, n-m, \alpha) = R(17, 754, 0.005) = 1.025$ $R(2, 754, 0.005) = 1.008$

$R_w(6)/R_w(9) = 1.003$
$R(1, 754, 0.005) = 1.006$

Table 6. *Bond lengths (Å) and valency angles in* HCB *as computed for model 6 and model 10*

Estimated standard deviations are given in parentheses. Single and double primes refer to positions $\bar{y}$, $x-y$, z and $y-x$, $\bar{x}$, z respectively.

	Model 6	Model 10
B(1)—N(2')	1·398 (8)	1·427 (8)
B(1)—N(2'')	1·451 (8)	1·427 (8)
B(1)—Cl(3)	1·724 (9)	1·735 (8)
N(2)—Cl(4)	1·749 (8)	1·736 (8)
Cl(3)—Cl(4')	3·181 (6)	3·162 (4)
Cl(3)—Cl(4'')	3·142 (7)	3·162 (4)
N(2')–B(1)–N(2'')	118·5 (1·0)	119·7 (0·4)
B(1')–N(2)–B(1'')	121·5 (1·0)	120·3 (1·4)
N(2)–B(1')–Cl(3')	120·1 (0·7)	120·2 (0·8)
N(2'')–B(1')–Cl(3')	121·3 (0·5)	120·2 (0·8)
B(1')–N(2)–Cl(4)	120·4 (0·5)	119·8 (0·8)
B(1'')–N(2)–Cl(4)	118·1 (0·6)	119·8 (0·8)

Table 4. *Vibrational parameters* (10^4 Å²) *for* HCB

The estimated standard deviations (10^4 Å²) are given in parentheses. Upper line: model 6; lower line: model 10. The temperature factor is defined as exp$[-2\pi^2 \sum_{i\ j} h_i h_j a_i^* a_j^* U_{ij}]$.

	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{13}$
B(1)	366 (22)	207 (15)	462 (24)	211 (28)	39 (26)	−87 (31)
	258 (16)	232 (15)	537 (32)	248 (23)	−60 (28)	−82 (35)
N(2)	308 (18)	524 (22)	507 (23)	429 (31)	−16 (31)	75 (27)
	414 (18)	495 (21)	445 (24)	380 (30)	84 (30)	93 (34)
Cl(1)	366 (6)	416 (6)	851 (11)	301 (9)	−31 (11)	44 (10)
	382 (7)	453 (5)	830 (11)	388 (8)	−20 (10)	36 (9)
Cl(4)	345 (6)	478 (8)	723 (8)	280 (10)	53 (11)	20 (10)
	332 (7)	454 (7)	737 (9)	191 (8)	5 (11)	25 (9)

Table 7. *Geometry of boron/nitrogen compounds*

Distances in Å units, valency angles in decimal degrees.

Compound	B–N(sh)	B–N(av)	B–N(1)	B–Cl	N–Cl	B–N–B	N–B–N
I	1·398 (8)	1·425	1·451 (8)	1·724 (5)	1·749 (8)	121·5	118·5
II	1·40 (3)	1·415	1·43 (3)	1·76 (3)	1·73 (2)	119	120
III	1·402 (11)	1·429	1·456 (11)				
IV	1·440 (16)	1·459	1·477 (16)				
V		1·413 (13)		1·760 (19)		120·8	118·5
VI		1·436 (2)				121·1	117·7
VII				1·73 (2)			
VIII				1·72 (3)			
IX					1·74 (2)		
X					1·77 (2)		

I   HCB (this paper);
II   HCB (Müller, 1971),
III   Tetra-*B*-isothiocyanato-tetra-*N*-butylborazocine (Clarke & Powell, 1966),
IV   Hexakis(trimethylsilyl)-2,4-diamino-1,3,2,4-diazodiboretidine (Hess, 1969).
V   Trichloroborazine (Coursen & Hoard, 1952),
VI   Borazine (Harshbarger, Lee, Porter & Bauer, 1969),
VII   Boron trichloride (Lévy & Brockway, 1937),
VIII   Phenyl borondichloride (Coffin & Bauer, 1955),
IX   Di-*N*-chloromethylamine (Skinner & Sutton, 1944),
X   *N*-Chlorodimethylamine (Skinner & Sutton, 1944).

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