

The Crystal Structure of Hexamethylenetetramine–Borine, $C_6H_{12}N_4 \cdot BH_3$

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The crystal structure of hexamethylenetetramine–borine has been determined by the three-dimensional X-ray method. The space group is $R3m$, lattice parameters: $a = 6.15 \pm 0.01 \text{ \AA}$ and $\alpha = 103.2 \pm 0.2^\circ$, with one formula in the unit cell; final refinement by a three-dimensional anisotropic least-squares analysis resulted in an R value of 6.8%. Hexamethylenetetramine–borine molecules have $C_{3v}-3m$ symmetry. The boron atom is bonded to one of the nitrogen atoms. Both atoms lie on the threefold rotation axis with a B–N separation of $1.661 \pm 0.007 \text{ \AA}$. The three nearest carbon atoms are arranged around the symmetry axis at a C–N distance of $1.527 \pm 0.005 \text{ \AA}$. Valence angles are: B–N–C, $111.5 \pm 0.3^\circ$; C–N–C, $107.4 \pm 0.3^\circ$. The length of the remaining C–N bonds in the molecule, $1.475 \pm 0.006 \text{ \AA}$, is in very close agreement with the C–N bond length, 1.476 \AA , found in hexamethylenetetramine itself. Valence angles, $\angle C-N-C = 108.2-108.5^\circ$ and $\angle N-C-N = 111.4-112.7^\circ$ are close to the tetrahedral value. The positions of hydrogen atoms were found by the three-dimensional difference Fourier synthesis. All hydrogen atoms are in the expected tetrahedral environments around the carbon and boron atoms. The BH_3 group has a staggered conformation with respect to the three nearest C–N vectors. The mean C–H and B–H bond lengths are 1.03 \AA and 1.08 \AA , respectively.

Introduction

The borine radical BH_3 is stable only in coordination compounds with electron-donor molecules. Lone-pair electrons of these molecules localized at the nitrogen, oxygen or carbon atoms can be used to complete an electron octet around the boron atom. The donor is in this case hexamethylenetetramine (known pharmacologically by other names such as urotropine).

Some qualitative information on the force constant and the bond order for the coordinative B–N bond were obtained from the vibrational spectra of $X_3B:NR_3$ ($X = H, CH_3, F, Cl, Br$; $R = H, CH_3$; Sawodny & Goubeau, 1965). The band which mainly represented the B–N vibrations was observed in the region 650 to 780 cm^{-1} . The value of the force constant was estimated by a normal coordinate treatment to be 2.3 to 3.4 mdyne \AA^{-1} . According to Siebert's (1953) formula the bond order is between 0.59 and 0.86.

The purpose of this work was to determine the molecular form, bond lengths and angles, electron density distribution, and molecular arrangement of the hexamethylenetetramine–borine complex, including the effect of interaction of permanent multipoles.

Experimental

Hexamethylenetetramine–borine crystals were kindly supplied by Dr J. Plešek. They were colourless, trans-

parent, elongated prisms of triangular cross-section. The unit-cell dimensions and space group data were obtained from Weissenberg, precession, rotation and powder photographs.

The unit cell of $C_6H_{12}N_4 \cdot BH_3$ is rhombohedral with dimensions:

$$a = 6.15 \pm 0.01 \text{ \AA} \quad \text{and} \quad \alpha = 103.2 \pm 0.2^\circ;$$

this corresponds to a hexagonal cell with:

$$a = 9.64 \pm 0.01 \text{ \AA} \quad \text{and} \quad c = 7.82 \pm 0.01 \text{ \AA}.$$

The measured density, $D_m = 1.26 \text{ g.cm}^{-3}$, corresponds to one molecule in the rhombohedral unit cell (the calculated density $D_x = 1.23 \text{ g.cm}^{-3}$).

Since there are no systematic absences with the rhombohedral indexing, and since the intensities of hkl and $h\bar{l}k$ intensities are equal within experimental error, the allowed space groups are: $R32$, $R3m$, and $R\bar{3}m$ (representing Laue symmetry $\bar{3}m$). However, space group $R32$ is ruled out since the complex cannot reasonably have D_3-32 symmetry.

The first structure model was obtained from the three-dimensional photographic data (156 independent reflexions) recorded on integrated Weissenberg films with $Cu K\alpha$ radiation with the equi-inclination technique (Hanic & Šubrtová, 1964). For the structure refinement, the intensities of 221 independent reflexions with rhombohedral indexing were collected with a Hilger & Watts automatic linear diffractometer using a scintillation counter, and $Mo K\alpha$ radiation. The crystal, of triangular cross-section with an edge length of

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0.3 mm, was mounted on the hexagonal *c* axis (prism axis). All the intensities were corrected for background. No absorption corrections were applied as X-ray absorption was negligible. Lorentz and polarization corrections were applied in the usual way. The different layers of *c* axis data were brought to a common scale by comparison with *Ok*l spectra. Wilson's (1942) method was used to bring the coefficients to an approximately absolute scale.

Determination of the structure

An initial model of the structure was obtained by interpretation of the three dimensional Patterson function. A set of trial coordinates was obtained assuming an undistorted hexamethylenetetramine molecule and a B-N separation of 1.58 Å (the expected length of the single bond). Successive structure factor and Fourier calculations reduced the *R*-index to 26%.

Further refinement of the parameters of the structure was carried out by a least-squares program of Daly, Stephens & Wheatley (1963) on an Elliot 803 computer. First, the coordinates and the individual isotropic temperature factors of all atoms except hydrogens, together with the overall scale factor, were refined. Five cycles of the block-diagonal anisotropic least-squares refinement, with 6 × 6 matrices for the thermal parameters, reduced the *R*-index to 0.093 and the residual $R' = \sum w|\Delta F|^2 / \sum wF_o^2$ to 0.020. A thermal factor of the form $\exp[-2\pi(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + \dots + 2U_{12}hka^*b^* + \dots)]$ was employed. In the least-squares calculations, the Cruickshank *et al.* (1961) weighting scheme was used.

The first structure refinement was performed in less than its full symmetry. The space group *R*3 was used for successive structure factor and Fourier calculations and to refine the structural parameters by least-squares with the separately estimated structure factors for *hkl* and *h $\bar{l}k$* . After five cycles of block-diagonal least-squares refinement, the maximum deviation of the atoms from the positions in the mirror plane was ±0.006 Å. Since these deviations were comparable with the standard deviations for atomic coordinates, and since indeed the *hkl* and *h $\bar{l}k$* structure factors were judged equal within experimental error, the positions of atoms in the mirror plane could be accepted (the *F_o* and *F_c* for the pairs *hkl* and *h $\bar{l}k$* anti-correlated about as often as they correlated, as regards the signs of the differences between the values for *hkl* and those for *h $\bar{l}k$*). When the hydrogen positions were fixed from the three-dimensional difference Fourier synthesis, structural parameters were further refined in the correct symmetry *R*3*m*. The block-diagonal least-squares refinement of all positional parameters was performed with constant anisotropic individual temperature factors. The hydrogen atoms were included in the refinement with temperature factors corresponding to the hydrogen-carrying carbon atoms. During the three cycles of least-squares refinement, the *R*-index was further reduced to 0.068 and the residual *R'* to 0.010. The values of the atomic parameters are given in Table 1 and those of the thermal parameters are given in Table 2. Table 3 shows the observed and the calculated structure factors obtained from the parameters in Tables 1 and 2. The bond lengths and angles and their standard deviations are given in Table 4.

Table 1. Final atomic coordinates, with standard deviations

		Coordinates					
Position		<i>x</i>	σ_x	<i>y</i>	σ_y	<i>z</i>	σ_z
B	(1 <i>a</i>)	0.0249	0.0010	0.0249	0.0010	0.0249	0.0010
N(1)	(1 <i>a</i>)	0.2366	0.0005	0.2366	0.0005	0.2366	0.0005
N(2)	(3 <i>b</i>)	0.4107	0.0007	0.4107	0.0007	0.6657	0.0007
C(1)	(3 <i>b</i>)	0.4780	0.0007	0.2228	0.0007	0.2228	0.0007
C(2)	(3 <i>b</i>)	0.6371	0.0008	0.6371	0.0008	0.3802	0.0008
H(1)	(3 <i>b</i>)	0.0195	0.0114	-0.1538	0.0115	0.0195	0.0114
H(2)	(3 <i>b</i>)	0.2411	0.0115	0.6699	0.0115	0.6699	0.0115
H(3)	(3 <i>b</i>)	0.4801	0.0107	0.7802	0.0106	0.7802	0.0106
H(4)	(6 <i>c</i>)	0.4849	0.0107	0.0642	0.0111	0.2348	0.0117

Table 2. Anisotropic thermal vibration matrix elements (Å²), with standard deviations

	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
B	0.056	0.056	0.056	0.028	0.028	0.028
σ	0.003	0.003	0.003	0.007	0.007	0.007
N(1)	0.039	0.039	0.039	0.021	0.021	0.021
σ	0.001	0.001	0.001	0.004	0.004	0.004
N(2)	0.062	0.062	0.048	0.026	0.029	0.029
σ	0.003	0.003	0.002	0.004	0.004	0.004
C(1)	0.047	0.050	0.050	0.024	0.024	0.030
σ	0.003	0.003	0.003	0.004	0.004	0.004
C(2)	0.050	0.050	0.057	0.016	0.025	0.025
σ	0.003	0.003	0.003	0.005	0.005	0.005

Discussion

The molecular symmetry of $C_6H_{12}N_4 \cdot BH_3$ is $C_{3v}-3m$. The B-N dative bond lies along the threefold rotation axis, the B-N bond length being 1.661 ± 0.007 Å. This value is comparable with the B-N interatomic distance of 1.62 Å found in $(CH_3)_3N \cdot BH_3$ by electron diffraction (Bauer, 1937) and with 1.64 ± 0.02 Å found in $CH_3CN \cdot BF_3$ by X-ray structure analysis (Hoard, Owen, Buzzell & Salmon, 1950). The B-N separations in $H_3N \cdot BF_3$ (Hoard, Geller & Cashin, 1951), $(CH_3)_3N \cdot BF_3$ (Geller & Hoard, 1951) and $(H_3C)_2N \cdot BF_3$ (Geller & Hoard, 1950) are slightly shorter, the bond lengths being 1.60, 1.585, and 1.57 Å, respectively. The expected length of a single bond from tetrahedral covalent radii ($r_B = 0.88$ Å and $r_N = 0.70$ Å) is 1.58 Å. The elongation of the B-N bond in the hexamethylenetetramine-borine molecule corresponds to the lower bond order of the B-N bond.

The remaining carbon and nitrogen atoms of the hexamethylenetetramine-borine molecule are in general positions. Two triads of the carbon atoms and one triad of the nitrogen atoms are related by the threefold rotation symmetry (Fig. 1). They form the globular remainder of the molecule. Two types of C-N bonds appear there. Three C(1) carbon atoms complete the tetrahedral arrangement around N(1) with C(1)-N(1) bond length of 1.527 ± 0.005 Å. The other C(1)-N(2) and C(2)-N(2) bond lengths are in very close agreement with C-N bond lengths, 1.476 ± 0.002 Å, found in the structure of hexamethylenetetramine itself by a low temperature X-ray study of cubic crystals (Becka & Cruickshank, 1963). While all C-N bonds are equivalent in the hexamethylenetetramine structure (the molecule possesses $\bar{4}3m$ symmetry), significant differences of the C-N bond lengths exist in the hexamethylenetetramine-borine molecule. Bond angles $\angle N-C-N$ are slightly larger than the valence angles $\angle C-N-C$. The molecular asymmetry is a result of the donated electron pair bond $\equiv N \rightarrow BH_3$.

The BH_3 -group has a staggered conformation with the three N(1)-C(1) vectors. All three hydrogens are in the expected tetrahedral environments around the

borine atom. The hydrogen atoms are at a B-H distance of 1.08 ± 0.07 Å. Two hydrogens complete the tetrahedral arrangement around each carbon atom with the C-H mean distance 1.03 ± 0.06 Å; this distance is somewhat shorter than the bond length C-H found in hexamethylenetetramine (1.088 Å, from neutron diffraction data; Anderson, 1957). The mean bond angles are $\angle H-C-H = 109.4^\circ$ and $\angle H-C-N = 109.8^\circ$.

The arrangement of the hexamethylenetetramine-borine molecules in the crystal structure is influenced by strong electric octupoles of the molecules, and the octupolar attraction makes the energy of the simple rhombohedral lattice lower than that of the close-

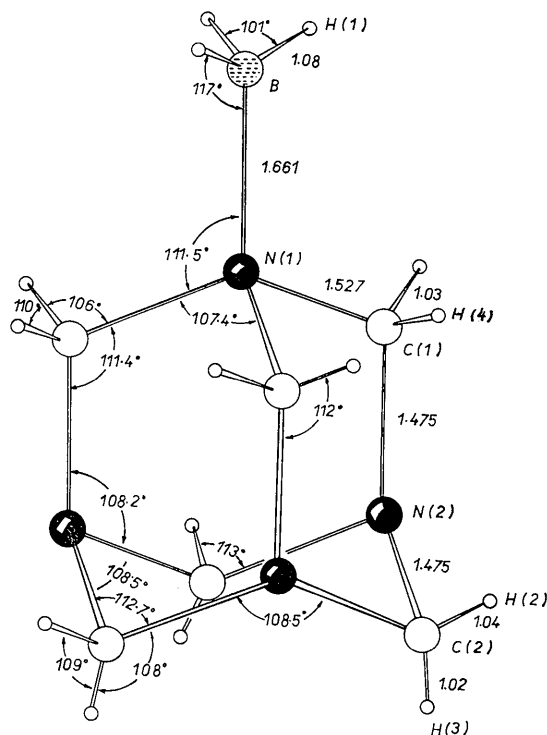


Fig. 1. The structure of the hexamethylenetetramine-borine molecule; final bond lengths and valence angles are indicated.

Table 4. Interatomic distances and bond angles

Bond	Distance (Å)	σ (Å)	Bonds	Angle	σ
B—N(1)	1.661	0.007	B—N(1)—C(1)	111.5°	0.3°
N(1)—C(1)	1.527	0.005	C(1)—N(1)—C(1)	107.4	0.3
C(1)—N(2)	1.475	0.006	N(1)—C(1)—N(2)	111.4	0.3
N(2)—C(2)	1.475	0.006	N(2)—C(2)—N(2)	112.7	0.3
B—H(1)	1.08	0.07	C(1)—N(2)—C(2)	108.2	0.3
C(1)—H(4)	1.03	0.06	C(2)—N(2)—C(2)	108.5	0.3
C(2)—H(2)	1.04	0.06	H(1)—B—H(1)	100.7	5.5
C(2)—H(3)	1.02	0.06	H(1)—B—N(1)	117.3	4.0
			H(4)—C(1)—H(4)	109.9	5.1
			H(4)—C(1)—N(1)	106.2	3.6
			H(4)—C(1)—N(2)	111.8	3.6
			H(2)—C(2)—H(3)	108.9	4.3
			H(2)—C(2)—N(2)	112.6	3.7
			H(3)—C(2)—N(2)	107.9	3.7

packed face centred lattice (Kihara, 1963). Such an arrangement allows the close approach of negative (nitrogen) atoms and positive groups (methylene groups) of molecules. The hexamethylenetetramine-borane molecules are approximately spherical except for the protrusion of the BH_3 groups. Each molecule is surrounded by six others parallel to it, at a distance of 6.15 \AA between centres. Six other molecules are at 7.64 \AA , and two molecules along the $[111]_{\text{rh}}$ are at 7.82 \AA . This arrangement is somewhat different from that found in hexamethylenetetramine crystals, where each molecule is surrounded by eight others at 6.08 \AA between centres and by six others at 7.02 \AA in a body centred lattice. The α_{rh} value corresponding to body centred cubic packing is $109^\circ 28'$ in comparison with $\alpha = 103^\circ 12'$ for the hexamethylenetetramine-borane crystals.

The nearest distance of C and N atoms from different molecules is 3.82 \AA ; between B and C atoms, 3.94 \AA . The closest approach of the molecular cores, however, is influenced by the nitrogen-to-hydrogen and hydrogen-to-hydrogen contacts of the neighbouring molecules. Forty one such contacts involving a single molecule exist up to the upper limit 3.2 \AA . These contacts most frequently occur with distances of $2.8\text{--}3.0 \text{ \AA}$ ($6\text{N}\cdots\text{H}$ and $27\text{H}\cdots\text{H}$ contacts).

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Crystal and Molecular Structure of a Brominated Isofenchone

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The constitution and configuration of the compound produced by hydrobromination of *trans* pinocarveol has been determined by X-ray diffraction methods, and confirmed as 6-bromoisofenchone. The crystals are orthorhombic, $P2_12_12_1$, with $a = 12.89$, $b = 11.37$, $c = 6.90 \text{ \AA}$; $Z = 4$. Three-dimensional least-squares refinement of 637 reflexions has given a structure ($R = 0.126$) with an average standard deviation of 0.03 \AA in C–C bonds and no significant departures from expected bond lengths. Despite the strain introduced by the keto group, the molecular skeleton is remarkably symmetrical about the median plane. The dihedral angle in each of the 5-membered rings is about 55° .

Introduction

Hartshorn & Wallis (1963) reported that hydrobromination of *trans*-pinocarveol (I) followed by oxidation produced a brominated isofenchone (II) through a rearrangement reaction. The molecular structure of the product was established by degradation methods and

neutron magnetic resonance spectroscopy, but no indication of the stereochemistry of the molecule was obtained. A knowledge of the position of the bromine atom relative to the ring system was essential for determination of the rearrangement mechanism. N.m.r. results suggested the *endo* configuration (I.R.C. McDonald, private communication) but full confirma-