X-Ray Crystal Structure Characterization of Cyclo(hexacyanoborane), $(BH_2CN)_6$

By **Andrew T. McPhail** * and **Dennis L. McFadden**, Paul M. Gross Chemical Laboratory, Duke University, Durham, North Carolina 27706, U.S.A.

The geometry of the title compound has been established by single-crystal *X*-ray analysis. Crystals are triclinic, space group $P\bar{1}$, with $a = 10.01(1)$, $b = 8.78(1)$, $c = 4.90(1)$ Å, $\alpha = 110.2(1)$, $\beta = 93.9(1)$, $\gamma = 70.5(1)°$, $Z = 1$. The structure was solved by direct methods and refined by full-matrix least-squares calculations to R 0.055 over 631 statistically significant reflections from diffractometer measurements. The centrosymmetric chair-like macrocyclic ring is disordered through being distributed over two orientations. Mean dimensions are: B–C (or N) 1.56, C≡N 1.14, B–H 1.14 Å; C–B–N 107.0°; B–B–B–B dihedral angle 59.6°.

PREPARATION and separation of a novel series of macrocyclic cyanoboranes $(BH_2CN)_n$, $n = 4$—9, was reported recently [1,2] and their characterization as cyclic oligomers was inferred from spectroscopic studies. We undertook an *X*-ray-diffraction study of a crystalline representative of this class, cyclohexacyanoborane $(BH_2CN)_6$, in order to verify its cyclic nature and to establish its detailed geometry.

EXPERIMENTAL

Moderately air-stable crystals of $(BH_2CN)_6$ were grown by sublimation *in vacuo* as clusters of needles elongated along the *c* axis.

Crystal Data.—$C_6H_{12}B_6N_6$, $M = 233.1$, m.p. 148 °C, Triclinic, $a = 10.04(1)$, $b = 8.78(1)$, $c = 4.90(1)$ Å, $\alpha = 110.2(1)$, $\beta = 93.9(1)$, $\gamma = 70.5(1)°$, $U = 381.4$ Å^3, $D_m = 1.00$, $Z = 1$, $D_c = 1.01$, $F(000) = 120$. Mo-K_α radiation, $\lambda = 0.7107$ Å; μ(Mo-K_α) = 0.66 cm^{-1}. Space group $P\bar{1}$ (C_i^1).

Crystallographic Measurements.—Preliminary unit-cell dimensions were obtained from rotation and Weissenberg photographs taken with Cu-K_α ($\lambda = 1.542$ Å) radiation and from precession photographs taken with Mo-K_α radiation. Three-dimensional diffraction data for the $hk0$—4 levels were recorded photographically by the equi-inclination multiple-film Weissenberg method (Cu-K_α radiation) from a crystal of dimensions *ca.* 0.20 × 0.20 × 1.20 mm, coated with lacquer to prevent decomposition in air. Intensities were estimated visually by comparison with a calibrated intensity scale and corrected for spot-shape variation, Lorentz and polarization effects to yield a total of 728 non-zero structure amplitudes.

The same crystal was later oriented to rotate with the $[01\bar{2}]$ direction parallel to the ϕ-axis of an Enraf-Nonius CAD-3 diffractometer and accurate cell parameters derived from the setting angles for 40 high-order reflections. Three-dimensional diffraction data were taken at room temperature (*ca.* 25 °C) with Zr-filtered Mo-K_α radiation. All unique accessible data having $2\theta < 50°$ were collected by the θ—2θ scanning technique as described previously [3] with a scan range $(2.0 + 0.5 \tan \theta)°$. The intensity of a strong standard reflection measured periodically during the data collection showed no significant variation. Lorentz and polarization corrections were applied to 631 reflections having $I > 2\sigma(I)$. Examination of the ϕ dependence of the intensity of a strong axial reflection measured at $\chi = 90°$ indicated that, as expected, absorption effects were insignificant.

Structure Analysis.—The structure was solved by direct phase-determining procedures using the photographic data and the MULTAN [4] series of programmes. Analysis of the $|E|$ values did not produce a clear distinction in favour of either of the statistical centrosymmetric or non-centrosymmetric distributions. The structure was treated initially as belonging to the non-centrosymmetric space group $P1$ which imposes no symmetry constraints upon the single molecule in the unit cell. The $|E|$ values for reflections with h odd were found to be systematically weak and were rescaled to give $\langle|E^2|\rangle = 1$ for both $h = 2n$ and $h = 2n + 1$ parity groups before their introduction into MULTAN. Reflections chosen by the program for the starting set were 111, $25\bar{2}$, 213, $2\bar{1}1$, 301, $4\bar{2}2$, and $60\bar{3}$. Application of the iterative procedures to derive phase constants for all reflections having $|E| > 1.1$ produced only two different solutions, the others representing equivalent solutions with alternative origin positions. When $|E|$ maps were evaluated using the phases from the different solutions, one proved to be trivial whereas the other revealed clearly all the positions of the non-hydrogen atoms. Carbon and nitrogen atoms were weighted as carbon and atomic positional and isotropic thermal parameters were refined by several cycles of full-matrix least-squares calculations to R 0.151. At this point the photographic-data set was replaced by the superior diffractometer data (R 0.150) which was used for all subsequent refinement. Pairs of atomic co-ordinates resulting from several further rounds of least-squares calculations which reduced R to 0.118 were clearly related by a centre of symmetry. Accordingly, the co-ordinates were averaged and all further refinement was based upon $P\bar{1}$ being the correct space group.

Hydrogen-atom positions were calculated and found to coincide with regions of significant positive electron density in a difference-Fourier synthesis. Following the inclusion of the hydrogen contributions, several further rounds of least-squares calculations during which positional and thermal parameters (boron, carbon, and nitrogen anisotropic, hydrogen isotropic) were varied decreased R to 0.079. Inspection of the thermal parameters still failed to permit any distinction to be made between the carbon and nitrogen atoms. It was therefore concluded that the structure was disordered and an average scattering factor curve $(f_C + f_N)/2$ was employed for these atoms. The refinement converged at R 0.055 following several more least-squares iterations. Final atomic co-ordinates and thermal parameters are given in Tables 1 and 2. Observed and calculated structure

---

[1] B. F. Spielvogel, R. F. Bratton, and C. G. Moreland, *J. Amer. Chem. Soc.*, 1972, **94**, 8597.

[2] R. F. Bratton, D. L. Denton, C. G. Moreland, and B. F. Spielvogel, to be published.

[3] D. L. McFadden and A. T. McPhail, *J.C.S. Dalton*, 1974, 363.

[4] G. Germain, P. Main, and M. M. Woolfson, *Acta Cryst.*, 1971, **A27**, 368.

TABLE 1

Fractional atomic co-ordinates (× 10^4) and anisotropic thermal parameters * (× 10^4), with estimated standard deviations in parentheses

Atom	x	y	z	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
B(1)	870(5)	1 756(6)	8 396(10)	209(6)	289(8)	693(20)	−103(12)	−115(20)	316(20)
CN(2)	−320(3)	2 870(4)	7 001(7)	175(3)	234(5)	666(16)	−144(6)	−37(13)	167(14)
CN(3)	−1 232(3)	3 697(4)	6 056(7)	164(3)	247(5)	694(16)	−138(6)	−19(13)	154(15)
B(4)	−2 475(5)	4 891(6)	4 849(11)	174(5)	254(8)	871(26)	−66(11)	−126(21)	186(24)
CN(5)	−3 076(3)	3 679(4)	2 372(7)	145(3)	263(5)	789(16)	−101(1)	−45(13)	313(14)
CN(6)	−3 527(3)	2 811(4)	508(7)	137(3)	277(5)	849(16)	−82(7)	−52(13)	398(14)
B(7)	−4 179(5)	1 653(7)	−1 993(12)	153(5)	334(9)	971(30)	−151(10)	−131(21)	255(28)
CN(8)	−2 947(3)	388(4)	−4 272(7)	169(3)	246(5)	815(17)	−156(6)	−254(13)	369(13)
CN(9)	−2 069(3)	−548(4)	−5 993(7)	182(3)	234(4)	761(15)	−163(6)	−250(13)	323(13)

* In the form: $B \sin^2\theta/\lambda^2 = b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl$.

factors are listed in Supplementary Publication No. SUP 21335 (5 pp., 1 microfiche).*

Scattering factors for non-hydrogen atoms were taken from ref. 5 [carbon and nitrogen $(f_C + f_N)/2$], and for hydrogen from ref. 6. In the least-squares calculations the weighting scheme employed was $\sqrt{w} = 1$ for $|F_o| \leqslant 3.0$ and $\sqrt{w} = 3.0/|F_o|$ for $|F_o| > 3.0$; $\Sigma w\Delta^2$ was minimized.

TABLE 2

Hydrogen atom fractional atomic co-ordinates (× 10^3) and isotropic thermal parameters, with estimated standard deviations in parentheses

Atom	x	y	z	B/Å^2
H(1α)	132(4)	268(5)	1 021(9)	9.3(12)
H(1β)	39(4)	95(5)	925(9)	8.8(10)
H(4α)	−208(4)	569(5)	376(10)	9.3(11)
H(4β)	−327(5)	568(6)	653(11)	11.3(15)
H(7α)	−492(6)	245(7)	−324(13)	12.3(16)
H(7β)	−448(5)	78(5)	−115(9)	9.8(13)

DISCUSSION

The X-ray analysis proves unequivocally that $(BH_2CN)_6$ exists as discrete cyclic oligomers in which the centrosymmetric eighteen-membered macrocyclic ring adopts a chair conformation with sides formed from approximately linear B–C–N–B rods of mean length 4.26 Å. A view of the molecule and the atom-numbering scheme are shown in Figure 1.

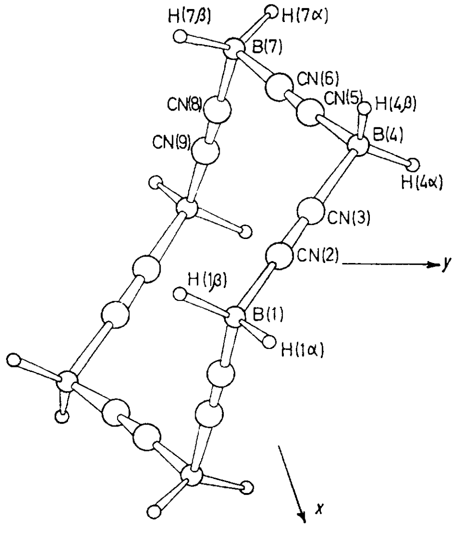

FIGURE 1 Molecular conformation and atom-numbering scheme

TABLE 3

Interatomic distances (Å) and angles (°), with estimated standard deviations in parentheses

(a) Bond lengths

B(1)–CN(2)	1.556(6)	CN(8)–CN(9)	1.141(5)
B(1)–CN(9^{I})	1.562(6)	B(1)–H(1α)	1.16(4)
CN(2)–CN(3)	1.145(5)	B(1)–H(1β)	1.17(4)
CN(3)–B(4)	1.568(6)	B(4)–H(4α)	1.19(5)
B(4)–CN(5)	1.552(6)	B(4)–H(4β)	1.06(5)
CN(5)–CN(6)	1.147(5)	B(7)–H(7α)	1.14(6)
CN(6)–B(7)	1.562(6)	B(7)–H(7β)	1.11(5)
B(7)–CN(8)	1.557(6)		

(b) Valency angles

CN(2)–B(1)–CN(9^{I})	107.9(3)	CN(9^{I})–B(1)–H(1β)	111(2)
B(1)–CN(2)–CN(3)	177.3(4)	H(1α)–B(1)–H(1β)	114(3)
CN(2)–CN(3)–B(4)	177.9(4)	CN(3)–B(4)–H(4α)	112(2)
CN(3)–B(4)–CN(5)	106.3(4)	CN(3)–B(4)–H(4β)	109(3)
B(4)–CN(5)–CN(6)	178.4(4)	CN(5)–B(4)–H(4α)	106(2)
CN(5)–CN(6)–B(7)	178.6(4)	CN(5)–B(4)–H(4β)	110(3)
CN(6)–B(7)–CN(8)	106.8(3)	H(4α)–B(4)–H(4β)	113(4)
B(7)–CN(8)–CN(9)	178.2(4)	CN(6)–B(7)–H(7α)	110(3)
CN(8)–CN(9)–B(1^{I})	177.2(4)	CN(6)–B(7)–H(7β)	109(2)
CN(2)–B(1)–H(1α)	108(2)	CN(8)–B(7)–H(7α)	103(3)
CN(2)–B(1)–H(1β)	108(2)	CN(8)–B(7)–H(7β)	102(2)
CN(9^{I})–B(1)–H(1α)	108(2)	H(7α)–B(7)–H(7β)	124(4)

(c) Intermolecular distances <3.5 Å

H(4β) · · · H($7\alpha^{\mathrm{II}}$)	2.84	CN(6) · · · H($4\beta^{\mathrm{IV}}$)	3.27
H(4α) · · · H($7\alpha^{\mathrm{II}}$)	2.95	H(4β) · · · H($7\beta^{\mathrm{IV}}$)	3.33
H(1α) · · · H($4\alpha^{\mathrm{III}}$)	3.04	B(1) · · · H($4\alpha^{\mathrm{III}}$)	3.35
B(4) · · · H($7\alpha^{\mathrm{II}}$)	3.14	B(7) · · · H($4\beta^{\mathrm{IV}}$)	3.44
CN(2) · · · H($4\alpha^{\mathrm{III}}$)	3.16	H(4β) · · · H($7\alpha^{\mathrm{IV}}$)	3.45
CN(5) · · · H($7\alpha^{\mathrm{II}}$)	3.22	H(1β) · · · CN(3^{VI})	3.49
H(4α) · · · CN(9^{V})	3.26		

(d) Torsion angles

B(1)–B(4)–B(7)–B(1^{I})	−58.4
B(4)–B(7)–B(1^{I})–B(4^{I})	60.1
B(7^{I})–B(1)–B(4)–B(7)	60.3

Roman numeral superscripts refer to the following transformations of the co-ordinates of Tables 1 and 2.

I $-x, -y, -z$
II $-1 - x, 1 - y, -z$
III $-x, 1 - y, 1 - z$
IV $-1 - x, 1 - y, 1 - z$
V $x, 1 + y, 1 + z$
VI $x, y, 1 + z$

Bond lengths and valency angles are in Table 3. The mean dimensions B–CN 1.56, C≡N 1.14, and B–H 1.14 Å are close to expected values.[7] The mean endocylic valency angle subtended at the boron atoms (107.0°) is

---

* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1974, Index issue.

[5] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

[6] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[7] *Chem. Soc. Special Publ.*, No. 11, 1958; No. 18, 1965.

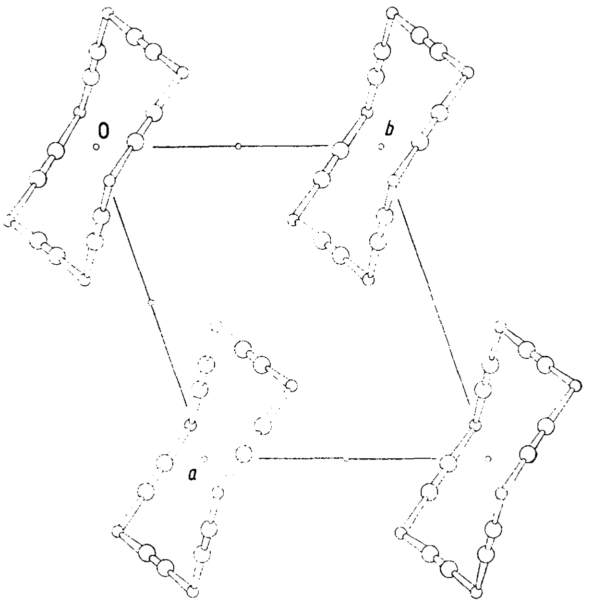

FIGURE 2 Packing in the crystal as viewed along the *c** axis

close to the ideal tetrahedral value (109° 28′), and consequently the mean B–B–B–B dihedral angle (59.6°) is not significantly different from the ideal (60°) for a regular chair conformation.

The arrangement of molecules in the crystal is shown in Figure 2. Intermolecular separations <3.5 Å (Table 3) all involve hydrogen atoms and correspond to normal van der Waals interactions. The similar values expected for B–C and B–N bond lengths, together with the weak intermolecular forces, produces conditions well suited for the structural disorder found here. Although further *X*-ray studies on other members of the series should permit the preferred ring conformations to be established these structures, too, would appear liable to similar disorder.

We thank the U.S. Army Research Office, Durham, for partial financial support, the U.S. National Science Foundation for funds for the purchase of the diffractometer, and Dr. B. F. Spielvogel for the crystals used in the analysis. Calculations were performed on an IBM 370/165 computer at the Triangle Universities Computation Centre, North Carolina.

[4/2635 *Received*, 17*th December*, 1974]