THE CRYSTAL AND MOLECULAR STRUCTURE OF 1,12-DIBROMO-1,2-DICARBA-*closo*-DODECABORANE 1,12-Br$_2$-1,2-C$_2$B$_{10}$H$_{10}$

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The structure of Br$_2$C$_2$B$_{10}$H$_{10}$ was determined by X-ray diffraction. The unit cell is tetragonal, space group $P4_1$, $a = 7.192(3)$ Å, $c = 21.374(8)$ Å, $Z = 4$. The bromine atoms are substituted on the orthocarborane cage in *para* position, one on the carbon atom in position 1 and second one on the boron atom in position 12. The final value of $R = 0.104$.

The purpose of this work was to solve the crystal and molecular structure of the new halogen derivate of orthocarborane, prepared by Plešek and Hanslík[1]. The compound originated as a product of direct bromination of 1-bromo derivative and by magnesylation and subsequent bromination of the 9-bromo derivative. Details about the synthesis were published[1].

The aim of the X-rays investigation was to determine at what position of the orthocarborane cage the two bromine atoms are substituted.

EXPERIMENTAL

Colourless, transparent crystals formed to cylindrical shape with the diameter 0.3 mm and length 0.55 mm were sealed into a Lindemann capillary.

From the preliminary investigation (Weissenberg goniometer, Cu$_{K\alpha}$ radiation) it was found, that this substance crystallizes in tetragonal symmetry. The absence of the 00*l* reflections for $l \neq 4n$ indicated the space group $P4_1$. This systematic extinction was confirmed in measuring the lattice parameters on the four-circle diffractometer (Hilger & Watts) with a scintillation counter and discriminator of impulses. Mo$_{K\alpha}$ radiation was used for all the measurements. The cell dimensions $a = 7.192 \pm 0.003$ Å, $c = 21.374 \pm 0.008$ Å were obtained by carefully measuring the scattering curves of the reflections of the type $h00$, $0k0$ and $00l$ and by determining the diffraction angles corresponding to their maxima. There are four molecules in a unit cell. The calculated density $d_c = 1.81$ g/cm^3 is in agreement with the experimental density $d_{exp} = 1.79$ g/cm^3 measured by flotation in a mixture of methyleneiodide and hexane at 20°C.

The experimental data were collected automatically. The ω-2ϑ scan was used for measuring of the integral intensities. The scan interval was 0.72°, the rate 1°/min. Background counts were taken for 18 s before and after scan. After each set of seven reflections the intensity of standard reflection was recorded. A slow and permanent decrease of the intensity of the standard reflection was noticed during the period of measuring, as the result of a slow decomposition of

TABLE I

Fractional Coordinates of the Atoms in the Molecule $1,12Br_2C_2B_{10}H_{10}$

Atom	x	y	z
Br 1	0·2565 (4)	0·5866 (4)	0·1651-fixed ($P4_1$)
Br 2	0·9295 (5)	0·2489 (5)	0·2537 (2)
C 1	0·4442 (25)	0·7607 (25)	0·1881 (12)
C 2	0·4077 (30)	0·9834 (30)	0·1798 (13)
B 3	0·3904 (27)	0·8937 (26)	0·2533 (15)
B 4	0·5655 (31)	0·7132 (33)	0·2551 (18)
B 5	0·6679 (28)	0·6990 (28)	0·1782 (14)
B 6	0·5561 (28)	0·8783 (30)	0·1312 (14)
B 7	0·5097 (32)	0·1088 (36)	0·2365 (16)
B 8	0·6106 (28)	0·9446 (29)	0·2876 (16)
B 9	0·7827 (27)	0·8229 (26)	0·2411 (15)
B 10	0·7742 (28)	0·9232 (27)	0·1635 (17)
B 11	0·6027 (27)	0·0950 (28)	0·1610 (17)
B 12	0·7427 (28)	0·0625 (27)	0·2287 (18)

TABLE II

Anisotropic Temperature Factors of the Individual Atoms and their Standard Deviations $\beta_{ij} . 10^4$

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Br 1	267 (7)	267 (7)	48 (2)	−22 (5)	−8 (2)	−5 (2)
Br 2	290 (8)	270 (8)	46 (2)	−37 (6)	−8 (3)	−6 (2)
C 1	112 (31)	146 (31)	20 (10)	0 (23)	−13 (12)	−13 (11)
C 2	194 (37)	136 (40)	35 (8)	32 (28)	−2 (14)	4 (14)
B 3	74 (30)	142 (30)	24 (9)	−39 (22)	−13 (12)	16 (13)
B 4	215 (39)	113 (37)	26 (10)	−1 (28)	−6 (17)	−5 (18)
B 5	137 (32)	114 (32)	15 (9)	25 (24)	−15 (13)	8 (12)
B 6	170 (34)	125 (34)	20 (10)	−19 (25)	18 (13)	16 (13)
B 7	137 (42)	128 (36)	29 (9)	−17 (29)	−3 (14)	8 (15)
B 8	118 (34)	147 (34)	21 (9)	20 (27)	−4 (13)	14 (14)
B 9	94 (30)	144 (30)	27 (8)	26 (23)	21 (12)	−2 (12)
B 10	141 (34)	118 (33)	15 (10)	−25 (25)	−5 (15)	1 (14)
B 11	135 (33)	124 (32)	31 (10)	22 (24)	12 (14)	−9 (14)
B 12	110 (35)	119 (34)	24 (11)	18 (26)	9 (11)	2 (12)

TABLE III

Fractional Coordinates of the Hydrogen Atoms

Atom	x	y	z
H 3	0·290	0·873	0·296
H 4	0·498	0·554	0·284
H 5	0·715	0·560	0·176
H 6	0·473	0·844	0·091
H 7	0·463	0·230	0·262
H 9	0·928	0·794	0·248
H 10	0·901	0·942	0·127
H 11	0·627	0·198	0·114

TABLE IV

Bond Distances in the Molecule $1,12\text{-Br}_2\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}$ (in Å)

Br 1 — C 1	1·91	B 5 — B 10	1·81
Br 2 — B 12	1·97	B 6 — B 10	1·74
		B 6 — B 11	1·72
C 1 — C 2	1·63	B 7 — B 8	1·77
		B 7 — B 11	1·75
C 1 — B 3	1·73	B 7 — B 12	1·72
C 1 — B 4	1·71	B 8 — B 9	1·81
C 1 — B 5	1·68	B 8 — B 12	1·79
C 1 — B 6	1·69	B 9 — B 10	1·81
C 2 — B 3	1·70	B 9 — B 12	1·77
C 2 — B 6	1·67	B 10 — B 11	1·75
C 2 — B 7	1·68	B 10 — B 12	1·73
C 2 — B 11	1·67	B 11 — B 12	1·78
B 3 — B 4	1·81	B 3 — H 3	1·17
B 3 — B 7	1·81	B 4 — H 4	1·39
B 3 — B 8	1·78	B 5 — H 5	1·06
B 4 — B 5	1·80	B 6 — H 6	1·08
B 4 — B 8	1·83	B 7 — H 7	1·08
B 4 — B 9	1·78	B 9 — H 9	1·08
B 5 — B 6	1·82	B 10 — H 10	1·21
B 5 — B 9	1·81	B 11 — H 11	1·26

TABLE V

Symmetric Pairs of Bond Lengths (in Å) and their Absolute Differences (in 0·01 Å)

C 1 — B 3	1·73	4	B 3 — B 8	1·78	4
C 1 — B 6	1·69		B 6 — B 10	1·74	
C 1 — B 4	1·71	3	B 4 — B 8	1·83	2
C 1 — B 5	1·68		B 5 — B 10	1·81	
C 2 — B 3	1·70	3	B 4 — B 9	1·78	3
C 2 — B 6	1·67		B 5 — B 9	1·81	
C 2 — B 7	1·68	1	B 7 — B 8	1·77	2
C 2 — B 11	1·67		B 10 — B 11	1·75	
B 3 — B 4	1·81	1	B 7 — B 12	1·72	6
B 5 — B 6	1·82		B 11 — B 12	1·78	
B 3 — B 7	1·81	9	B 8 — B 9	1·81	0
B 6 — B 11	1·72		B 9 — B 10	1·81	
			B 8 — B 12	1·79	6
			B 10 — B 12	1·73	

the crystal under X-rays. That is why two crystals had been used for data collection. A total of 5503 intensities of individual reflections were measured. Backgrounds were substracted and intensities were placed on a common scale with the help of the standard reflection. Symmetrically equivalent reflections were averaged and some unreliable of them were eliminated. Intensities were then corrected for Lorentz, polarisation and absorption factors (calculated absorption correction coefficient for the size of sample and $Mo_{K\alpha}$ radiation is $\mu R = 1·16$ with $\mu = 77·11$ cm^{-1}). After all these corrections we had a set of 1252 independent structure factors, of which 194 were zero. To these we assigned the value $1/2$ F_0 min.

Structure Determination

The structure was solved by the heavy atom method. Analysis of the three-dimensional Patterson function yielded the coordinates of the two bromine atoms. From the Fourier synthesis phased only by bromine contribution the positions of all non-hydrogen atoms and their icosahedral arrangement were established. It was found, that bromine atoms are substituted on the carborane cage at *para* positions. After two subsequent cycles of Fourier synthesis more precise positions of atoms were found but it was not yet possible to distinguish the carbon atoms from boron atoms. The *R*-factor was 0·226.

The positions and isotropic temperature factors of all nonhydrogen atoms were then refined by the method of least squares (local version of Bussing and Levy program[2]). But the structure did not refine well and we considered it as a consequence of the errors in the determination of intensities caused by the decomposition of crystals. From the computations up to this stage we recognized, that the value of the intensity of the standard reflection (corresponding to the degree of deterioration of the sample) may serve as a criterion for estimating the reliability of the observed intensities. That is why we divided the set of the reflections into seven classes in dependence upon the value of the standard reflection and introduced seven scale factors. Some reflections measured with low intensity of standard reflection were deleted, some others were included after

a revision of the original measuring records. As a result of these corrections we obtained a set of 1 262 reflections.

In several cycles the coordinates, the isotropic temperature factors and scale factors were refined and the *R*-factor decreased to $R = 0.122$. During the refinement Cruickshank's weight was used instead of $w = 1/\sigma^2$ and the number of reflections which were involved in further cycles of isotropic refinement was 765.

The determination of the carbon atoms was achieved during the refinement. The C 1 atom on which the bromine atom Br 1 is bonded was identified in one of two possible opposite positions in the carborane cage from the changes of value of the isotropic temperature factor and from the known fact, that the distance Br-C is shorter than the distance Br-B.

For the determination of the second carbon atom we used (besides of the changes of the isotropic temperature factors) some additional criteria, *viz.*: the average values of the bond length of all atoms to their five nearest neighbours, the average values of the *meta* distances and the *para* distances in the carborane cage. Moreover we made a comparison of the carborane cage with a regular icosahedron the edge of which had length 1.79 Å, placed so that the sum of squares of the distances between the corresponding vertices of the icosahedron and the real cage was minimum. We searched for an atom, the position of which was markedly more inside the cage than the position of the other ones. Such an atom was found — in agreement with all criteria mentioned above — and identified as C 2. Moreover assuming that the orthocarborane cage has symmetry C_s, *i.e.* that there is a mirror plane, defined by the points C 1, B 12 and the neighbour of C 1, we made a check of symmetry for all five possible positions of the mirror plane in calculating the differences of symmetrically corresponding bond lengths. We found that the differences were minimal for the plane, defined by the C 1, B 12 and the atom, identified as C 2.

The last cycles of isotropic refinement were computed with two carbon and ten boron atoms in the carborane cage and the determination of the structure was closed by computing one cycle of anisotropic refinement, where the *R*-factor decreased to 0.104. From the ten hydrogen atoms only eight were located from the Fourier and difference Fourier synthesis. Their coordinates which were not included to the refinement are listed in Table III. The structure factors Table is available from authors on request.

The calculations were performed on the computer Tesla 200 in the Institute of Solid State Physics using local programs.
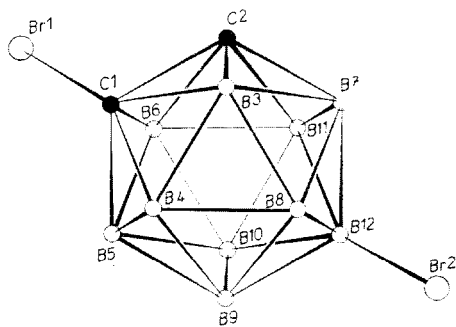

FIG. 1

Arrangement of the Whole Molecule of $1,12\text{-Br}_2\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}$

RESULTS AND DISCUSSION

Fig. 1 shows the whole molecule. The coordinates and standard deviations of the Br, B, and C atoms are listed in Table I. In Table II the coefficients β_{ij} of the anisotropic temperature factor: $\exp\left(-\left(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl\right)\right)$ are given. The atoms were numbered according the numbering convention used for icosahedral structures[3].

As may be seen from Fig. 1. one bromine atom is substituted on the carbon atom in position 1 with the bond length 1·91 Å and the second one on the boron atom in *para* position 12. Br—B distance was found to be 1·97 Å. All distances in the orthocarborane cage are given in Table IV. The B—B distances range from 1·72 Å to 1·83 Å and their mean value is 1·78 Å. The C—B distances are from 1·67 Å to 1·73 Å and their mean value is 1·69 Å. The C—C distance was found to be equal 1·63 Å. Bond distances of the hydrogen atoms to the corresponding boron atoms
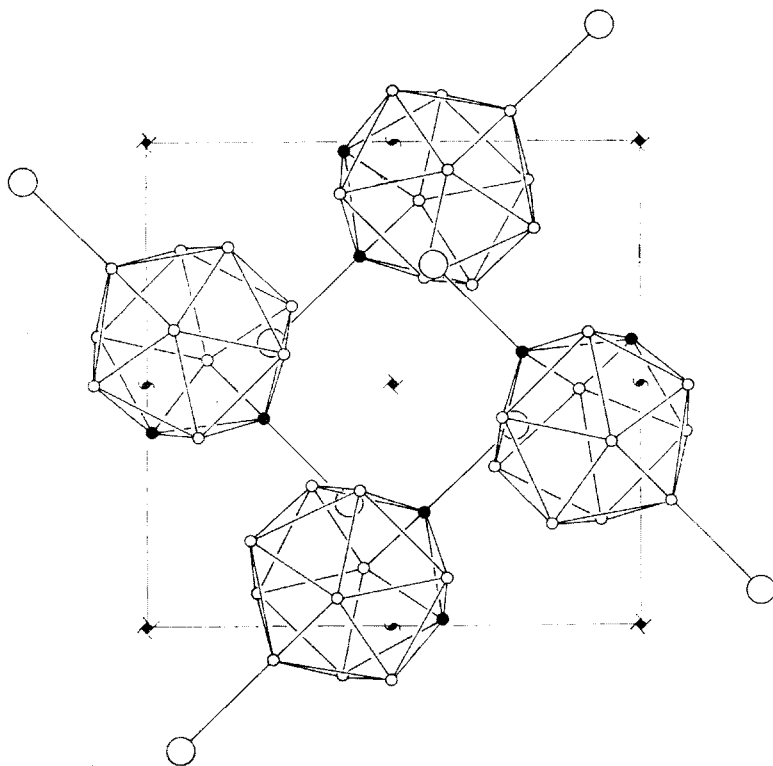

FIG. 2

Arrangement of the Molecules of Dibromo-dicarba-dodecaborane in the Tetragonal Unit Cell

range from $1.06\ Å - 1.39\ Å$, the mean distance B—H is $1.17\ Å$. The numbering of the hydrogen atoms is identical with the numbering of the boron atoms to which these hydrogen atoms are bound. All interatomic bond lengths are in good agreement with the corresponding values previously reported for similar compounds.

The molecule is nearly C_s symmetric with respect to the plane defined by C 1, C 2 and B 12. The deviations from symmetry are given in Table V as absolute differences (in $0.01\ Å$) between the symmetrically corresponding bond lengths. The least intermolecular distance is H 4 — H 7 equal to $2.39\ Å$.

Fig. 2 shows the arrangement of the molecules of dibromo-dicarba-dodecaborane in the tetragonal unit cell.

REFERENCES

1. Plešek J., Hanslik T.: This Journal *38*, 335 (1973).
2. Busing W. R., Martin K. O., Levy H. A.: *A Fortran Crystallographic Least-Squares Program.* Oak Ridge National Laboratory, Oak Ridge, Tennesee 1962.
3. Hart H. V., Lipscomb W. N.: Inorg. Chem. *12*, 2645 (1973).