Electron Diffraction Determination of the Molecular Structure of 1,6-Dicarba-*closo*-hexaborane(6)

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Summary. The molecular structure of 1,6-dicarba-*closo*-hexaborane(6), 1,6-$C_2B_4H_6$, has been determined in the vapour phase by electron diffraction.

STRUCTURAL investigations of small carboranes and their derivatives have been undertaken in the microwave studies of 2,4-$C_2B_5H_7$,[1] 1,2-$C_2B_4H_6$,[2] and 2-Cl-1,6-$C_2B_4H_5$.[3] Theoretical works[4–6] have made use of these experimental results, although theoretical predictions first appeared some years ago.[7] We started an electron diffraction investigation of 1,6-$C_2B_4H_6$ in order to obtain additional values for the B–B and B–C distances in a simple compound which cannot be studied by microwave spectroscopy because it has no dipole moment.

The sample used for the diffraction experiments was prepared by the published procedure[8] and its purity (99%) checked by i.r. and mass spectrometry.[9] A range of $3{\cdot}2 < s < 31{\cdot}0$ was covered. The sample container was cooled to $-50°$. The molecular parameters have been refined by least-squares method with a diagonal weight-matrix using the program of H. M. Seip.[10].

The simplest model of D_{4h} symmetry was assumed for 1,6-$C_2B_4H_6$ (Figure) in agreement with the ^{11}B and ^1H n.m.r. and i.r. spectra.[9] The molecular structure is described by four parameters: the C–H, B–H, B–B, and B–C bond distances. A satisfactory fit was achieved when the three geometrical parameters and some grouped non-bonded amplitudes were varied. Values obtained were B–H 1·15(3), B–B 1·725(12), and B–C 1·635(4) Å; a value for C–H of 1·11 Å was assumed; $R = 0{\cdot}075$ The e.s.d.s were obtained by multiplying the original standard deviations calculated by the least-squares program by a factor of three

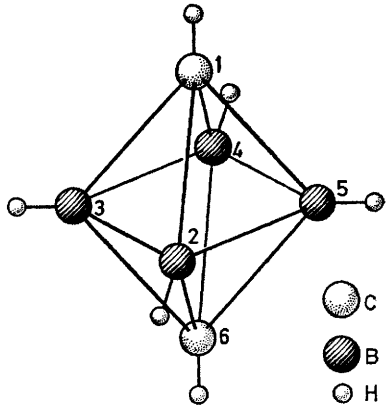

FIGURE. *Structure of* 1,6-*dicarba*-closo-*hexaborane* (6).

o compensate for correlation of intensity data.[11] The tructural parameters given are $r_g(1)$[12] and are not corrected or shrinkage. For the bonded and non-bonded amplitudes easonable values were obtained in the refinement.

The results reported here confirm an octahedral (tetra-gonal bipyramidal) arrangement of atoms in a C_2B_4 cage, as uggested earlier[9] and found in the isoelectronic ion $B_6H_6^{2-}$.[13]

The B–C bond distance is similar to the mean values of 1·61 Å in 2-Cl-1,6-$C_2B_4H_5$[2] and 1·616 Å in 1,2-$C_2B_4H_6$.[3]

Another comparison can be made for molecules in which the carbon atom has different co-ordination numbers (n_C): $n_C = 4$ in BMe_3,[14] B–C = 1·578 Å, $n_C = 5$ in 1,6-$C_2B_4H_6$, B–C = 1·635 Å, and $n_C = 6$ in 1,12-$C_2B_{10}H_{12}$,[15] B–C = 1·710 Å. In these cases the B–C bonds obeyed with reasonable accuracy the following empirical rule: $r(BC) = (1{\cdot}311 + 0{\cdot}066\, n_C)$ Å. This conclusion is in agreement with the CNDO/2 calculations[5] made for some carboranes.

The B–B bond distance is in reasonable conformity with the mean values reported for related molecules: 1·686 in 2-Cl-1,6-$C_2B_4H_5$,[2] 1·69 in $B_6H_6^{2-}$,[13] and 1·736 in Å1,2-$C_2B_4H_6$.[3]

After this study was completed Prof. S. H. Bauer (Cornell University, Ithaca, USA) sent us the results of his investigation of the same molecule. Our values agree within a few thousands of an angstrom for the B–B and B–C bond distances. For C–H and B–H he reports 1·104 and 1·244 Å, respectively.

(*Received, 22nd February* 1973; Com. 249.)

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