Determination of the Molecular Structure of $C_4B_2H_6$ by Microwave Spectroscopy

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Summary The molecular structure of $C_4B_2H_6$ is shown to be a pentagonal pyramid with olefinic C–C bonding by rotational spectroscopy.

WE report the results of our structural determination of the carborane, 2,3,4,5-tetracarbahexaborane(6), $C_4B_2H_6$. This compound has the highest ratio of carbon to boron in its skeleton of any known carborane. It was prepared by pyrolysis of 1,2-tetramethylenediborane(6) at 550°[1] and also by the reaction of acetylene and 1,2-$C_2B_3H_7$ at 50° C.[2] We have determined that $C_4B_2H_6$ has the form of a pentagonal pyramid with the molecular structure shown in the Figure. The four carbons are situated in the base of the pyramid. In particular, the short C–C bond lengths should be noted.

Proton and boron n.m.r. and i.r. measurements on $C_4B_2H_6$[1] have shown that the two boron nuclei are not symmetrically equivalent; that there are two pairs of equivalent carbon atoms; that there are no bridge hydrogens; and that the carbon atoms might be olefinic in nature. The pentagonal pyramid structure is consistent with these data.

We have determined the structure by using standard microwave spectroscopic methods. The rotational spectra of 10 isotopic species have been analysed. The boron isotopes were studied in natural abundance. The ^{13}C isotopes were synthesized by using HC≡CH enriched with 60% ^{13}C. All of the heavy atoms have been accurately located.

From the analysis of the isotopic species the co-ordinates were determined by the Kraitchman method[3] by using eight isotopic species as the reference molecules. Whenever appropriate a C_s symmetry plane including B(1) and B(6) was assumed. When the symmetry of the molecule was broken by ^{13}C substitution at either C(2) or C(3), the principal axes were rotated up to 35°. When the substituted atom was located near a principal plane, imaginary values were often obtained for the co-ordinates owing to zero-point vibrational effects. These data were not used in obtaining the final results. Sufficient data with different standard reference species were available to determine unambiguously the signs of all co-ordinates except the *c*-co-ordinate of C(2). This ambiguity is indicated by using both a +ve and −ve value for the C(2) *c*-co-ordinate in the Table.

TABLE. The atomic co-ordinates in $C_4B_2H_6$ in the principal axis system of the normal isotopic species.[a]

	Co-ordinates (Å)		
Atom	*a*	*b*	*c*
B(1)	−0·082 ± 0·013	0·00[b]	0·989 ± 0·003
C(2)	0·370 ± 0·006	1·1905±0·002	−0·152 ± 0·04 +0·138 ± 0·03
C(3)	−0·979 ± 0·004	0·712±0·005	−0·263 ± 0·02
B(6)	1·344 ± 0·002	0·00[b]	−0·248 ± 0·003

[a] C_s symmetry has been assumed. [b] Assumed to be on the plane of symmetry.

A direct comparison of the co-ordinates obtained by using different isotopes as reference species was not usually possible because such isotopic substitution shifted the centre of mass, and rotated the principal axes significantly. Since atoms were often situated near an axis, only two isotopic reference species were useful in obtaining direct values for the bond lengths. Such an approach ignored most of the data and yielded little information about the accuracy of the results. Hence, the co-ordinates obtained in each of the eight reference systems were readjusted to the principal axis system of the normal species and averaged. In this way all the available data could be used for the final structural determination. The final results are given in the Table. The probable errors given in this Table were calculated by using the deviations from the mean co-ordinates. A complete description of the method will be published elsewhere.

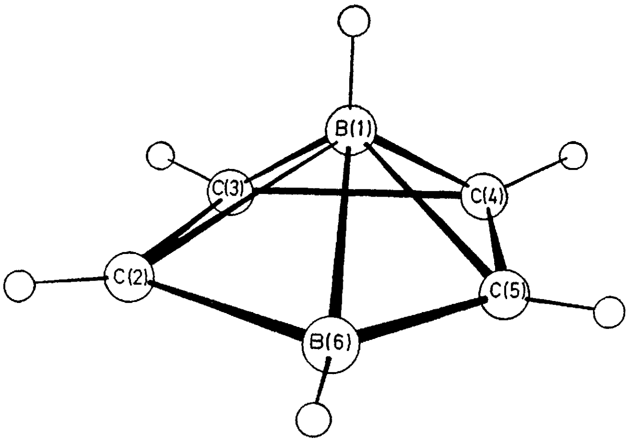

FIGURE. Molecular structure of $C_4B_2H_6$.

Bond lengths (Å)

B(1)–B(6)	1·886 ± 0·003
B(1)–C(2)	1·709 ± 0·003 (1·531)
B(1)–C(3)	1·697 ± 0·015
B(6)–C(2)	1·541 ± 0·007 (1·585)
C(2)–C(3)	1·436 ± 0·008 (1·486)
C(3)–C(4)	1·424 ± 0·007

The bond lengths given in the Figure were readily obtained from the average co-ordinates. The choice between two final structures depends upon the undetermined sign of the *c*-co-ordinate of C(2). The choice of a negative sign is favoured because the positive sign leads to a C–B bond length of 1·53Å, which is unrealistically short for an apex to base bond. The results using a positive sign are given in parentheses.

All the basal bond lengths are very short even though the cage structure is electron deficient. The short C–C bonds of 1·44 Å compare with 1·48 Å for the C–C bond in butadiene[4] and 1·397 Å in benzene[5] while the C–B bond of 1·54 Å is comparable to 1·60 Å in CB_3BF_2[6] or 1·56 Å in $C_2B_5H_7$.[7] Also, the base is similar to the cyclopentadienyl unit found in organometallic compounds. Thus, this compound might be considered as a π–bonded compound with the apex boron replacing the usual metal ligand.

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