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Skeletal Molecular Structure of Monocarbahexaborane from Microwave Spectral Studies

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Summary Analysis of the microwave spectrum shows the skeletal molecular structure of CB_5H_7 to be a distorted octahedral form with a face containing three long B–B bonds, and there is further evidence that a hydrogen atom is located in or above the octahedral face.

THE first one-carbon carborane to be synthesized was CB_5H_7 and it is the only known closo-carborane containing a hydrogen bridge. Onak, Drake, and Dunks[1] initially prepared the compound from 1-methylpentaborane using a silent electrical discharge. They deduced the symmetry by ^{11}B and ^{1}H n.m.r. and i.r. spectral analyses and inferred that the molecule is octahedral. Chemical evidence by Prince and Schaeffer[2] indicated the presence of a single bridge hydrogen and supported the octahedral structure. The exact position of the hydrogen bridge is unknown and could conceivably be located (a) in an equatorial position, (b) between an apex and an equatorial site, or (c) in an octahedral face. Although Onak, *et al.* preferred a structure where the bridge proton lies between B(2) and B(3), an alternative structure in terms of n.m.r. spectral evidence is given by a rapidly tautomerizing hydrogen bridge between B(2) and B(6). Since it is likely that such a tautomeric possibility would be 'frozen' on a GHz time scale, it was felt that the microwave structural determination would be able to differentiate unambiguously between the possible configurations.

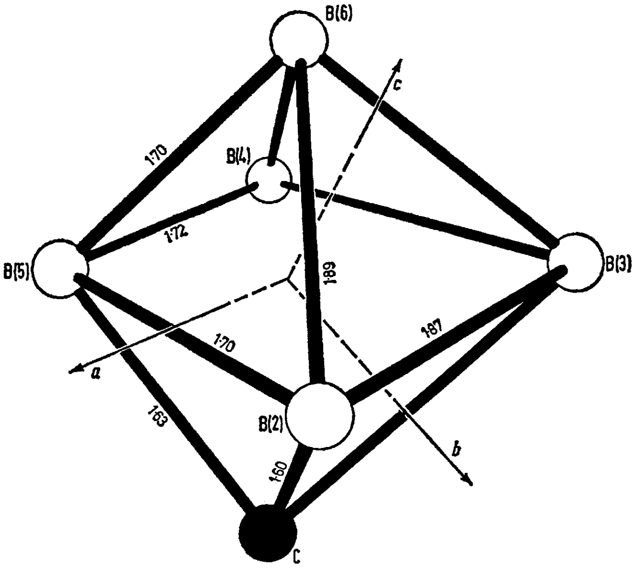

FIGURE. Molecular structure of CB_5H_7.

Both weak *R*-branch and much stronger *Q*-branch lines were observed in the region from 8–40 GHz. Low-*J* *R*-branch transitions of four isotopic species were observed and assigned on the basis of Stark effects. From the measurement of relative line intensities, the isotopic abundances were determined to be in the ratio of 4:2:2:1. This is consistent both with the expected isotopic abundances for a molecule with a plane of symmetry bisecting the B(2)–B(3) and B(4)–B(6) distances and containing B(6), and with the n.m.r. evidence showing two equivalent sets of boron atoms. Kraitchman's method[3] was employed to determine the co-ordinates of the boron atoms in the principal axis frame of the parent molecule. It has been determined that the molecule possesses large *b*-dipole and small *c*-dipole components, so the symmetry plane must necessarily lie in the *bc* inertial axis plane. Since a substitution of ^{10}B at B(2) or B(4) is equivalent to a substitution at B(3) or B(5), respectively, these pairs of atomic positions differ only in the sign of the distance along the *a*-axis. The zero *a*-component for a substitution at B(6) is noted.

A similar analysis of a ^{13}C enriched sample not only determined the carbon co-ordinates but also unambiguously determined the sign of the *c*-co-ordinates of the equatorial borons by the isotope pulling method.[4] The co-ordinates of all atoms in the principal axis frame of the parent and the ^{13}C substituted molecule are shown (Figure).

Though essentially of octahedral form the structure is considerably distorted with one face containing three long B–B distances. This arrangement correlates with the idea of a hydrogen bridge in the face, proposed by Onak, *et. al.*[1] as the best explanation for the n.m.r. observations. Our CNDO calculations also indicate that the structure with a hydrogen located above the octahedral face bounded by the three long B–B bonds is 28 kcal mol^{-1} more stable than the structures with an equatorially bridged hydrogen.

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[1] T. Onak, R. Drake, and G. Dunks, *J. Amer. Chem. Soc.*, **1965**, **87**, 2505.
[2] S. R. Prince and R. Schaeffer, *Chem. Comm.*, **1968**, **451**.
[3] J. Kraitchmann, *Amer. J. Phys.*, **1953**, **21**, **17**.
[4] E. Grozek, J. B. Leach, G. T. F. Wong, C. Ungermann, and T. Onak, *Inorg. Chem.*, **1971**, **10**, **2770**.