

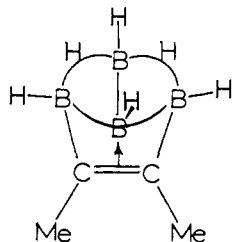
Molecular Structure of $B_4H_6C_2(CH_3)_2$

Sir:

We report the first detailed structure, established by low temperature single-crystal X-ray diffraction methods, of a compound,¹ $B_4H_6C_2(CH_3)_2$, in which both B and C are present as part of the polyhedral-like framework, and in which C is in an unusual electron-deficient bonding situation. The two C atoms are adjacent, and therefore no transformation to a presumably more stable structure² has occurred. This compound is geometrically analogous to B_6H_{10} ,³ but a significant difference is required in the valence description when the H_bB-BH_b unit having nearly tetrahedral H-bridged B is replaced by the C-C unit having nearly trigonally bonded C. Nearly trigonal hybridization about nonmethyl C atoms is supported by bond angles $4'45 = 121^\circ$, $543 = 122^\circ$ and $4'43 = 115^\circ$, and by the surprisingly short C-C distance of 1.432 Å., about the same as that of 1.42 Å. in graphite, and intermediate between the 1.50 Å. sp^2-sp^2 single bonded⁴ and 1.34 Å. double bonded⁵ distances (Fig. 1).

A molecular orbital analysis of the simpler, but analogous, $B_4H_6C_2H_2$ molecule has yielded bond orders and charge distributions as defined by Mulliken, and obtained previously⁶ from an extended LCAO-MO Hückel theory for compounds of boron and carbon. The bond order of 0.96 for the 1.432 Å. C-C distance lies on the bond order-distance line determined by C_2H_4 , C_6H_6 , and C_2H_6 . The B-C bond order of 0.85 for the 1.520 Å. bond, slightly greater than that of 0.74 for $B(CH_3)_3$ assuming $B-C = 1.52$ Å., is thus effectively that of a single bond, strengthened perhaps by some electron delocalization. On the other hand, the B-C bond 1-4 of 1.76 Å. length has a bond order of only 0.30, partly because it is longer but also partly because of unfavorable bond angles relative to the strong bonds to atom 4.

Our best localized bond description starts with all atoms neutral and a double bond between 4 and 4'. Donation from the π bond is then allowed along the arrow toward an available sp^2 orbital of the apex B atom 1.



This π -donation model stresses the sp^2 bonding geometry of the nonmethyl C atoms more satisfactorily than do the previous proposals.^{1,2}

The LCAO-MO charge distributions superimpose on this description a typically exaggerated charge displacement, suggesting charges of -0.43 on 4, 0.33 on 1, 0.25 on 2, 0.12 on 3, and 0.02 on 9. We expect that a deeper study would make bridge H atoms negative, and B atoms 1 and 2 less positive. Nevertheless, the symmetrical bonding of the apex B and the expected ring current would allow its B^{11} n.m.r. signal to appear at highest field.

We do not wish to imply that C-C distances in other

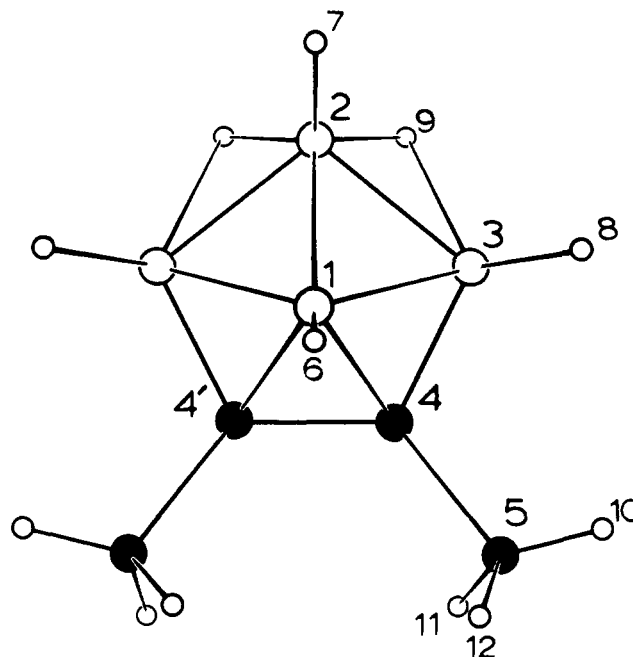


Fig. 1.—Molecular structure of $B_4H_6C_2(CH_3)_2$. Black circles are C atoms, large open circles are B atoms, and small circles are H atoms. The C-C distance between atoms 4 and 4' is only 1.432 Å. Other bond distances are 1-2 = 1.705, 1-3 = 1.768, 1-4 = 1.762, 2-3 = 1.778, 3-4 = 1.520, and 4-5 = 1.506 Å. Distances involving H are 2-9 = 1.38 and 3-9 = 1.28 for bridge atom 9, 1.29 (av.) for B-H (terminal) and 0.97 (av.) for C-H distances. Standard deviations are about 0.005 Å. for B-B and C-C distances and just under 0.1 Å for B-H or C-H distances.

polyhedral-like molecules containing both B and C will be as remarkably small, partly because the analogous B-B distance in B_6H_{10} is, by far, the shortest in all of the boron hydrides. Therefore, further structural studies will be required in order to provide a more adequate experimental basis for charge distribution among atoms of these kinds of molecules.

Parameters for the LCAO-MO studies are -15.20 (B_{2s}), -8.50 (B_{2p}), -21.40 (C_{2s}), and -11.40 (C_{2p}) in e.v. for the Coulomb integrals α_i . The resonance integrals were taken as $\beta = (K/2)(\alpha_i + \alpha_j)S_{ij}$, where S_{ij} is the integral based upon Slater orbitals with the usual exponents,⁶ and $K = 1.75$.

The crystallographic results indicated two molecules in a unit cell based upon the space group $P2_1nm$ and having dimensions $a = 5.709$, $b = 6.046$, and $c = 10.556$ Å. The disagreement factor for all 470 reflections is $R = \sum |F_o| - |F_c| / \sum |F_o| = 0.08$.

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Cyclopropane Radical Anion¹

Sir:

A detailed molecular orbital calculation² on cyclopropane based on the experimental data of Muller and

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(2) K. W. Bowers and F. D. Greene, to be published.