## 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 structure[2] 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 $4'45 = 121°$, $543 = 122°$ and $4'43 = 115°$, 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 bonded[4] and 1.34 Å. double bonded[5] 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 previously[6] 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.
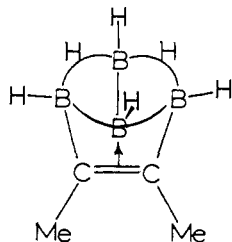
This π-donation model stresses the sp^2 bonding geometry of the nonmethyl C atoms more satisfactorily than do the previous proposals.[1,2]

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

(1) T. P. Onak, R. E. Williams, and H. G. Weiss, *J. Am. Chem. Soc.*, **84**, 2830 (1962).

(2) R. Hoffmann and W. N. Lipscomb, *Inorg. Chem.*, **2**, 231 (1963).

(3) F. L. Hirshfeld, K. Eriks, R. E. Dickerson, and E. L. Lippert, Jr., *J. Chem. Phys.*, **28**, 56 (1958).

(4) C. A. Coulson, Volume commératif Victor Henri, Desoer, Liège, 1948.

(5) J. M. Dowling and B. P. Stoicheff, *Can. J. Phys.*, **37**, 703 (1959).

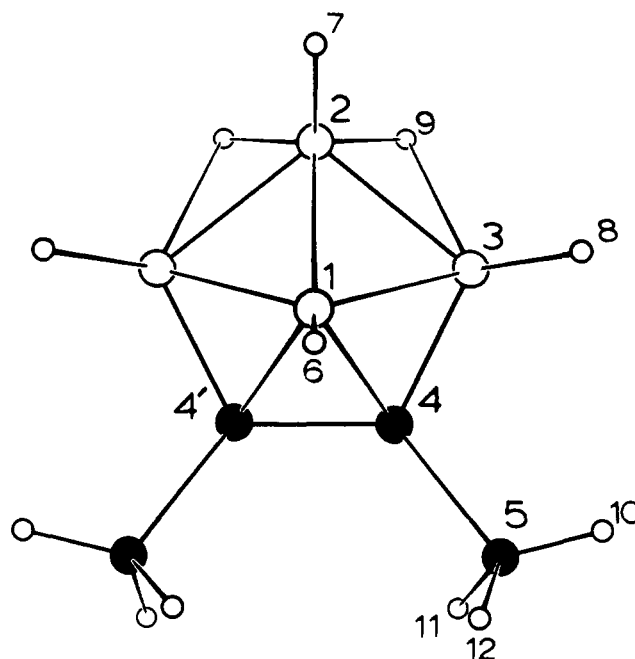(6) R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, **37**, 2872 (1962).

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 $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.08$.

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Cyclopropane Radical Anion[1]

Sir:

A detailed molecular orbital calculation[2] on cyclopropane based on the experimental data of Muller and

(1) This work was supported under Contract No. AT(30-1)-905 with the Atomic Energy Commission. Reproduction is permitted for any purpose of the United States Government.

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

Pritchard[3] and Flygare, Narath and Gwinn[4] suggested the possibility of formation of the radical anion. The electron spin resonance spectrum of cyclopropane radical anion now has been observed.[5]

Sodium metal[6] in tetrahydrofuran[7] produced no observable resonance signal from cyclopropane. Sodium in dimethoxyethane[7] produced a weak signal, inadequate to obtain fine structure. Potassium and rubidium metals separately in dimethoxyethane produced signals of higher intensity, and some fine structure could be observed. The use of a sodium–potassium alloy in 2:1 tetrahydrofuran–dimethoxyethane at $-168°$[8] produced a completely resolved spectrum consisting of seven lines of binomial intensity ($1:6:15:20:15:6:1$) as expected for interaction with six equivalent protons. The separation between lines is 2.33 gauss with a line width of 0.44 gauss.[9] The g-factor is 2.0027. Calibration was by means of peroxylamine disulfonate. The spectrum disappears on warming to $-100°$ but reappears on cooling again.

The work on cyclopropanes is being avidly continued and is being extended to other systems.[10]

(3) N. Muller and D. E. Pritchard, J. Chem. Phys., 31, 768 (1959).

(4) W. H. Flygare, A. Narath and W. D. Gwinn, ibid., 36, 200 (1961).

(5) A Varian Associates V-4500 spectrometer with 100 kc. modulation was used for this work.

(6) The metals were distilled directly into the quartz sample tubes on a high vacuum line.

(7) Solvents were purified exhaustively until a blue solution of potassium could be supported for many days at room temperature.

(8) J. R. Bolton, Mol. Phys., 6, 219 (1963).

(9) Variation in line width (presumably due to electron exchange with free cyclopropane) and in intensity occurs from sample to sample but the separation between lines is constant at 2.33 gauss.

(10) NOTE ADDED IN PROOF.—Since submission, a number of systems have been observed to present hazard. Some sample tubes have burst with considerable violence even though sealed under high vacuum and stored in liquid nitrogen. The lifetimes vary from minutes to days depending on the compound used.

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Mössbauer Resonance Effects in Iron⁰ Organometallic Complexes

Sir:

We wish to report the Fe^{57} Mössbauer resonance[1] absorption results of a series of diene–iron tricarbonyl complexes and dienyl–iron tricarbonyl complex cations. In common with most other iron compounds, the Mössbauer spectra of these materials consist of two absorption lines of equal intensity. The pertinent data are listed in Table I. The center of gravity of the two lines (δ) and the separation (Δ) are given in millimeters per second.[2]

Group I compounds consist of the neutral diene–iron tricarbonyls, group II contains the salts of the dienyl–iron tricarbonyl cations, while $Fe(CO)_5$ and $Fe(CO)_3(PPh_3)_2$ are listed together as group III. The data for $Fe(CO)_5$[3] and for cyclooctatetraene–iron tricarbonyl[4] have been reported. Our data on splittings agree, but a comparison of the absolute chemical shift is clouded by lack of accepted standards.

It is seen from Table I that the diene–iron tricarbonyl complexes show strong quadrupole splitting and possess a chemical shift within the fairly narrow region $\delta = 0.2$

(1) An excellent introduction to the subject is H. Frauenfelder, "The Mössbauer Effect," W. A. Benjamin Co., New York, N. Y., 1962.

(2) Natural abundance Fe⁵⁷ proved adequate for these studies. A copper–cobalt⁵⁷ source was utilized at room temperature in a constant velocity servo-controlled loudspeaker drive system. Spectra were all obtained at 78°K. on thin samples (40–80 mg./cm.²). Type 302 stainless steel absorbs, at room temperature, at −0.325 mm./sec. relative to this Cu–Co⁵⁷ source.

(3) L. M. Epstein, J. Chem. Phys., 36, 2731 (1962).

(4) G. K. Wertheim and R. H. Herber, J. Am. Chem. Soc., 84, 2274 (1962).

TABLE I

MÖSSBAUER PARAMETERS FOR VARIOUS IRON ORGANOMETALLIC COMPLEXES

Group I

	δ_{Cu}, mm./ sec.	Δ, mm./ sec.
2-Methoxy-3,5-hexadiene–Fe(CO)₃	−0.218	1.71
racemic-5,6-Dimethyl-1,3,7,9-tetradecaene–Fe₂(CO)₆	−.216	1.69
Alloocimine–Fe(CO)₃	−.214	1.75
meso-5,6-Dimethyl-1,3,7,9-tetradecaene–Fe₂(CO)₆	−.208	1.58
2-Hydroxy-3,5-hexadiene–Fe(CO)₃	−.202	1.56
Butadiene–Fe(CO)₃	−.198	1.46
7-Acetoxy-bicycloheptadiene–Fe(CO)₃	−.191	2.01
1-Phenylbutadiene–Fe(CO)₃	−.178	1.59
2,4-Hexadienoic acid–Fe(CO)₃	−.178	1.63
Cyclooctatetraene–Fe(CO)₃	−.140	1.26

Group II

1,5-Dimethylpentadienyl–Fe(CO)₃⁺BF₄⁻	−0.126	1.83
1-Methyl-pentadienyl–Fe(CO)₃⁺SbCl₆⁻	−.126	1.69
Cyclohexadienyl–Fe(CO)₃⁺ClO₄⁻	−.122	1.66
1-Methyl-pentadienyl–Fe(CO)₃⁺ClO₄⁻	−.117	1.70
1-Methyl-pentadienyl–Fe(CO)₃⁺BF₄⁻	−.117	1.72
Cycloheptadienyl–Fe(CO)₃⁺BF₄⁻	−.111	1.57
1-Methyl-pentadienyl–Fe(CO)₃⁺PF₆⁻	−.103	1.67
Bicyclooctadienyl–Fe(CO)₃⁺BF₄⁻	−.098	1.79

Group III

Bistriphenylphosphine–Fe(CO)₃	−0.324	2.76
Iron pentacarbonyl	−0.282	2.60

$\pm$ 0.025 mm./sec. The range of ligands in complexes listed include non-conjugated dienes and substituted dienes as well as tetraene–diiron hexacarbonyl complexes; this range might therefore be considered characteristic of such complexes. The notable exception in group I is cyclooctatetraene–iron tricarbonyl; both in chemical shift and quadrupole splitting this substance appears to be abnormal. The reasons for these deviations are not yet clear. The shift for cyclooctatetraene–[Fe(CO)₃]₂ is 0.05 mm./sec. less,[4] which places it in a "normal" position.

These shifts are small compared to those of inorganic salts which, at 78°K., typically give $\delta = +0.35$ for Fe^{3+}, $\delta = +1.20$ for Fe^{2+},[5] and $\delta = -1.0$ for Fe^{6+},[6] converted to the Cu–Co⁵⁷ source.

The cationic complexes listed in group II clearly form a separate group based upon their chemical shift, though they display roughly the same range of quadrupole splitting as seen in the diene–iron tricarbonyl complexes. In contrast to ferrocinium salts,[3,7] the chemical shift and quadrupole splitting of salts of the 1-methylpentadienyl–iron tricarbonyl cation are relatively insensitive to the nature of the anion.

The cations absorb at higher values than do the diene–Fe(CO)₃ complexes; however, the effect is small and certainly would not seem large enough to support the suggestion[8] that these complexes be regarded now as Fe^{2+} systems containing a carbanion as a ligand. Even considered as Fe⁰ systems bonded to a carbonium ion ligand, the differences between group II complexes and group I complexes seem small. The mean difference in chemical shift between the two is 0.09 mm./sec. Epstein[9] has shown that a difference of 0.04 mm./sec. exists between tris-5-nitrophenanthroline and tris-

(5) S. DeBenedetti, G. Lang, and R. Ingalls, Phys. Rev. Letters, 6, 60 (1961).

(6) G. K. Wertheim and R. H. Herber, J. Chem. Phys., 36, 2497 (1962).

(7) G. K. Wertheim and R. H. Herber, ibid., 38, 2106 (1963).

(8) E. O. Fischer and R. D. Fischer, Angew. Chem., 72, 919 (1960).

(9) L. M. Epstein, paper delivered at the 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April 1, 1963.