those triangles furthest from the C atoms, and also to give different weights to the *ortho–meta* path (A) than to the *ortho–ortho* paths (BCDE) in order to fit the unusual features of the observed product distribution. For example, if rotation by 120° of those triangles which break the fewest B–C bonds is allowed to occur preferentially (4, 8, 9; 7, 8, 12; 5, 9, 10; 10, 11, 12 in A; 8, 9, 12 in B and D; and 9, 10, 12 in C and E) and if path A is given 10%[6b] of the weight and the other 90% is divided equally among BCD and E, the calculated yields are 63, 31, 1, 0, 1, 3, 1, and 0% after one step and 0, 0, 0, 0, 23, 28, 35, and 14% after many steps of this mechanism (products are listed in the order 9-Br-*o*, 8-Br-*o*, 4-Br-*o*, 3-Br-*o*, 9-Br-*m*, 5-Br-*m*, 4-Br-*m*, 2-Br-*m*). Yields for intermediate times are reproduced almost as well.

Other derivatives (such as 8-Br-*o*, 4-Br-*o*, and 3-Br-*o*, separated from isomerization mixtures of 9-Br-*o*) have also been subjected to these rearrangements. The same general mechanism is found to apply but with some small changes in the weighting of the *ortho–meta* pathways and with some other changes in the restrictions of triangle rotations probably associated in an interesting way with differences in bonding in these isomers.

Further studies are under way on more complex systems, and at higher temperatures, at which *para* compounds are produced upon further transformations of *meta* isomers.

Table I. Yields (per cent) for the Rearrangements of 9-Bromo-*o*-carborane at 420–425°

| | Time, min | | | |
Product	30	60	210	330
9-Br-*o*	68	52	20	0
8-Br-*o*	21	23	14	0
4-Br-*o*	3	8	8	0
3-Br-*o*	0	1	4	0
9-Br-*m*	3	6	15	24
5-Br-*m*	4	7	18	28
4-Br-*m*	1	3	17	35
2-Br-*m*	0	0	4	13

(9) On leave from the University of California at Los Angeles, Los Angeles, Calif.

H. D. Kaesz,[9] R. Bau, H. A. Beall, W. N. Lipscomb

*Department of Chemistry, Harvard University
Cambridge, Massachusetts 02138*
Received June 7, 1967

metry in B_8Cl_8 requires that two different types of B atoms in $B_6H_6C_2(CH_3)_2$ have a coincident [11]B resonance in the spectrum taken at 12.8 Mc. This coincidence remains in the 19.3-Mc [11]B nmr spectrum, which led to some favoritism[3] for the structure derived from the Archimedian antiprism of D_{4d} symmetry for an equal-atom structure; however, the ambiguity of this conclusion was recognized, and study of the [11]B nmr spectrum at still higher resolution was recommended.[3] A dynamical structure, fluctuating between these, is also a possibility,[4] but now seems less likely in view of the higher temperatures normally required for polyhedral carborane rearrangements. Also, and finally, one type of intermediate structure which has only one square face is plausible,[4] and we shall show that the actual structure has very slight distortions toward this intermediate. Also, we establish with certainty the positions of the carbon atoms in the B_6C_2 polyhedron.

Results were obtained from three-dimensional X-ray diffraction data obtained from a single crystal at about −50°. The space group is C2/c, and there are four molecules in a unit cell having parameters $a = 15.24$, $b = 5.89$, $c = 12.74$; $\beta = 131.4°$. The structure, solved from Sayre's equations[5] (in a modified form of the multiple-solution program of Long[6]), has yielded a value of $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.11$ for 491 observed reflections. The molecule (Figure 1) has C_2 symmetry, coincident with a crystallographic C_2 axis. The B_6C_2 polyhedron is based upon the same idealized polyhedron as was found in B_8Cl_8, and shown[4] to have satisfactory molecular orbitals for both B_8H_8 (D_{2d}) and $B_8H_8^{2-}$ (D_{2d}). The C atoms are separated from one another and in the positions expected for greatest stability in their interactions with the molecular orbitals. Thus it is probable that less stable isomers can occur if preparative methods are less drastic. The distances are comparable in a general way with those[2] in the B_8Cl_8 polyhedron: bonds at atomic sites having smaller number of coordination tend to be shorter, and the shortest distances are the 1, 2 and 7, 8 distances, whereas the longest distances are between adjacent pairs among the 3, 4, 5, and 6 atoms in both B_8Cl_8 and $B_6H_6C_2(CH_3)_2$.

The smaller covalent radius of C is probably a major factor which appears to shorten distances near carbon atoms. The larger nuclear charge on C, as compared to B, appears to withdraw electrons from the adjacent B atoms, and the relatively long B_3–B_4 distance of 1.89 ± 0.01 A is directly comparable with less precisely established distances of 1.89 ± 0.04 A in m-$B_{10}Br_2H_8C_2H_2$[7] and 1.89 ± 0.06 A in m-$B_{10}Cl_{10}C_2H_2$[8] for a bond between B atoms each joined to two C atoms. However, in the molecule $B_7H_7C_2(CH_3)_2$ of C_{2v} symmetry (like $B_9H_9^{-2}$ of D_{3h} symmetry) this type of B–B distance is

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Structure of the Carborane $B_6H_6C_2(CH_3)_2$

Sir:

Of the polyhedral carborane structures, $B_6H_6C_2H_2$, which we study here as its C,C'-dimethyl derivative, is of uncertain structure. The interpretation[1] of the [11]B nuclear magnetic resonance (nmr) spectrum on the basis of the polyhedron established[2] to have D_{2d} sym-

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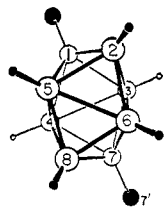(8) J. A. Potenza and W. N. Lipscomb, *Proc. Natl. Acad. Sci. U. S.*, **56**, 1917 (1966).

Figure 1. The structure of $B_8H_8C_2(CH_3)_2$. Methyl groups at 1' and 7' are attached to carbon atoms 1 and 7, respectively. Bond distances (all ±0.01 A) are $C_1-B_2 = 1.50$, $C_1-B_3 = 1.70$, $C_1-B_4 = 1.60$, $C_1-B_5 = 1.70$, $B_2-B_3 = 1.77$, $B_2-B_5 = 1.81$, $B_2-B_6 = 1.70$, $B_3-B_4 = 1.89$, $B_3-B_6 = 1.84$, and $B_5-B_6 = 1.90$ A. The B_2-B_8 distance is 2.87 A while the C_1-C_7 distance is 2.60 A. Other distances are related to these by the molecular twofold axis.

Figure 1. Plot of absorbance (at 372.5 mμ, the isosbestic point for o-nitrophenol and o-nitrophenolate) vs. time for the reaction of bovine ribonuclease-A with o-nitrophenyl hydrogen oxalate anion ($4.45 \times 10^{-4} M$) at 30°; pH 5.9 in 0.1 M collidine perchlorate buffer (O, enzyme = $3.08 \times 10^{-5} M$; △, enzyme = $2.2 \times 10^{-5} M$; O, no enzyme).

1.76 A.[9] It is even more interesting that the B_3-B_4 and B_5-B_6 distances of 1.89 and 1.90 A, respectively, are more than five standard deviations longer than the 1.84-A distances, B_3-B_6 and B_4-B_5. Thus there appears to be a tendency for both the $C_1B_3B_4C_7$ unit [$(C_1-C_7)/(B_3-B_4) = 1.37$] and the $B_2B_5B_8B_6$ unit [$(B_2-B_8)/(B_5-B_6) = 1.51$] to deviate slightly toward a squarelike shape, as compared with the idealized ratio of 1.62 from, for example, an icosahedron.

Molecular orbital calculations will be presented in the full paper after revision of our program to new methods[10] and after determination of other carborane structures. All previous molecular orbital studies have been carried out on idealized geometries; it will probably be of importance to reexamine these molecules theoretically when detailed geometries become available.

NOTE ADDED IN PROOF. The geometry of $B_8H_8^{2-}$, which is isoelectronic with $B_6H_6C_2H_2$, has been described by F. Klanberg, D. R. Eaton, L. J. Guggenberger, and E. L. Muetterties [*Inorg. Chem.*, 6, 1271 (1967)]. The geometry and distortions from regular distances are like those found in B_8Cl_8 which has consistently been described as a molecule of D_{2d} symmetry (see ref 2).

Acknowledgment. We wish to thank M. F. Hawthorne for the sample, the Office of Naval Research for support of the research, and the National Science Foundation for a fellowship to H. V. H.

(9) T. F. Koetzle, F. E. Scarborough, and W. N. Lipscomb, submitted for publication. The framework C atoms in $B_7H_7C_2(CH_3)_2$ are at two of the three apical positions, which are each coordinated to four B atoms.
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H. V. Hart, W. N. Lipscomb
*Department of Chemistry, Harvard University
Cambridge, Massachusetts 02138*
Received June 7, 1967

The Reaction of Ribonuclease-A with o-Nitrophenyl Hydrogen Oxalate

Sir:

We report herein the initial results of our study of the reaction of o-nitrophenyl hydrogen oxalate anion (o-NPO⁻) with RNase.[1] The reaction of p-nitrophenyl acetate with RNase has, in our hands as well as in those

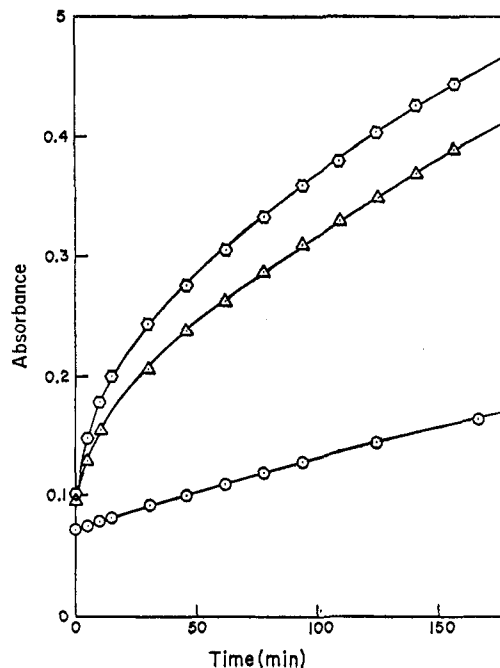(1) For the rational leading to this study see T. C. Bruice and B. Holmquist, *J. Am. Chem. Soc.*, 89, 4028 (1967).

of Ross and co-workers,[2] been found to be a very slow reaction comparable to the nonenzymic reaction of this ester with insulin.[3] In contrast the reaction of RNase with the negatively charged o-NPO⁻ proceeds in two parts (Figure 1): (1) an "initial burst" which is first order in both enzyme and substrate following Lineweaver-Burk kinetics; and (2) a slower liberation of o-nitrophenol in a nonenzymic bimolecular reaction of protein and substrate to completion of hydrolysis. Extrapolation of the initial-burst reaction to zero buffer provides $K_{m(app)} = 1.25 \times 10^{-3} M$ and $k_{cat} = 0.31$ min⁻¹.[4] Comparison of $K_{m(app)}$ and k_{cat} for o-NPO⁻ to the values for cytidine 2',3'-cyclic phosphate[5,6] indicates that the apparent binding constant for the cyclic phosphate ester is approximately four times greater and k_{cat} 100 times greater than the corresponding constants for o-NPO⁻ (with acetate buffer $K_m = 3 \times 10^{-4} M$ and $k_{cat} = 39$ min⁻¹ for the cyclic phosphate ester).

For the reaction of the RNase derivative S-protein,[7] $K_{m(app)}$ was found to be the same as for RNase while k_{cat} was found to be decreased by 40%. For Asp₅₃ converted to methyl ester $K_{m(app)}$ also remains the same as for RNase, but k_{cat} is decreased by but 20%. Completely reduced RNase with all sulfhydryl groups carboxymethylated and RNase with all S-S bonds oxidized

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