CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT,
REACTION MOTORS DIVISION, THIOKOL CHEMICAL
CORPORATION, DENVILLE, NEW JERSEY

Carborane Derivatives. An Eight-Membered Exocycle of 1,2-Dicarbaclovododecaborane(12)

BY NATHAN MAYES AND JOSEPH GREEN

The syntheses of five- and seven-membered carborane[1] exocycles, in which one carborane participates in the ring, have been reported.[2,3] We wish to report now such an exocycle which has eight members. This compound, 1,4-dioxa-6,7-(1,2-carboranylene)-2-(1'-carboranyl)-2-methylcyclooctane, is a condensation product of 1-(epoxyisopropyl)carborane[4] and 1,2-bis-(hydroxymethyl)carborane.[5] The condensation yielded, in addition to the cyclooctane, the linear ether, β-hydroxy-β-(carboran-1-yl)propyl-(1'-hydroxymethylcarboran-2'-yl)methyl ether. The linear ether is probably an intermediate of the cyclooctane; however, this was not proven by independently converting the linear compound to the cyclic compound.

The preparation and probable structures of these compounds are illustrated in the equation below.
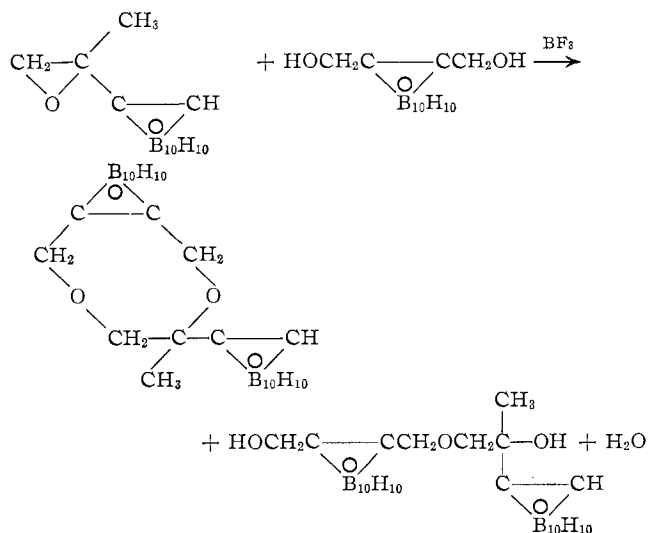
Experimental

1-(Epoxyisopropyl)carborane (26.0 g., 0.130 mole), 1,2-bis(hydroxymethyl)carborane (26.0 g., 0.127 mole), and 150 ml. of toluene were placed in a reaction flask fitted with a water condenser, a Dean–Stark distilling receiver, a Teflon-coated magnetic stirrer, and a gas inlet tube. The mixture was heated with stirring to reflux and became homogeneous. Boron trifluoride was bubbled into the solution several times during 48 hr. of refluxing, and 2.0 ml. of water was collected in the Dean–

Stark receiver. The reaction mixture was concentrated by evaporating most of the solvent and then dissolved in methanol and precipitated by addition of water. The solid precipitate weighed 19.5 g. (40% yield); a sample twice recrystallized from hexane melted at 249–251°. Infrared analysis, molecular weight determination, and elemental analysis indicated the compound to be 1,4-dioxa-6,7-(1,2-carboranylene)-2-(1'-carboranyl)-2-methylcyclooctane. The infrared spectrum contained absorptions at 3060 cm.⁻¹ for CH of carborane, at 2560 cm.⁻¹ for BH of carborane, at 1374 cm.⁻¹ for CCH$_3$, at 1127 cm.⁻¹ for COC, and at 730 cm.⁻¹ for BH deformation of carborane. No absorption for OH was present. The molecular weight obtained cryoscopically in benzene was 378 (calculated 386). *Anal.* Calcd. for C$_9$H$_{30}$O$_2$B$_{20}$: C, 27.96; H, 7.82; B, 55.93. Found: C, 26.77; H, 7.92; B, 55.72.

The methanol–water mother liquor was evaporated to yield a gum from which unreacted 1,2-bis(hydroxymethyl)carborane was extracted with 5% aqueous sodium hydroxide and unreacted 1-(epoxyisopropenyl)carborane was extracted with petroleum ether. The remaining solid, weight 9.6 g. (19% yield), was identified as β-hydroxy-β-(carboran-1-yl)propyl-(1'-hydroxymethylcarboran-2'-yl)methyl ether. After three recrystallizations from heptane it melted at 196–201°. The infrared spectrum exhibited absorption bands at 3370 cm.⁻¹ for OH stretching and a doublet at 1170 and 1160 cm.⁻¹ for tertiary OH deformation. Other bands were at 3080 cm.⁻¹ for CH of carborane, at 2940 and 2860 cm.⁻¹ for aliphatic CH, at 2560 cm.⁻¹ for BH of carborane, at 1116 cm.⁻¹ for COC, and at 727 cm.⁻¹ for BH deformation of carborane. The molecular weight determined cryoscopically in benzene was 415 (calculated 405). The proton magnetic resonance spectrum, obtained in benzene solution with tetramethylsilane added as an internal reference, exhibited the following singlets (τ): 8.95, CH$_3$; 7.18, CH$_2$; 6.89, tertiary OH; 6.72, CH$_2$; and 6.26, –CB$_{10}$H$_{10}$CH. The CH$_2$OH group appeared as an AB$_2$ multiplet with the center of the CH$_2$ doublet at τ 6.56 and the center of the OH triplet at τ 8.01. The first-order coupling constant was 7.9 c.p.s. The error for all values, except the –CB$_{10}$H$_{10}$CH shift, is ±0.01 p.p.m. The –CB$_{10}$H$_{10}$CH shift error is greater due to its unusually broad resonance. *Anal.* Calcd. for C$_9$H$_{32}$O$_3$B$_{20}$: C, 26.71; H, 7.97; B, 53.44; OH, 8.40. Found: C, 26.95; H 8.09; B, 51.34; OH, 8.92.

(1) The term "carborane" is used here to denote 1,2-dicarbaclovododecaborane(12).

(2) S. Papetti, B. B. Schaefer, H. J. Troscianiec, and T. L. Heying, *Inorg. Chem.*, **3**, 1444 (1964).

(3) J. Green, N. Mayes, A. P. Kotloby, and M. S. Cohen, *J. Polymer Sci.*, **A2**, 3135 (1964).

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(5) M. M. Fein, D. Grafstein, J. E. Paustian, J. Bobinski, B. M. Lichstein, N. Mayes, N. S. Schwartz, and M. S. Cohen, *ibid.*, **2**, 1115 (1963).

CONTRIBUTION FROM INORGANIC MATERIALS DIVISION,
NATIONAL BUREAU OF STANDARDS, WASHINGTON 25, D. C.,
AND DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF MARYLAND, COLLEGE PARK, MARYLAND

Additional Observations on the Electronic Spectrum of Copper(II) Acetate Monohydrate

BY CURT W. REIMANN,[1a] GERALD F. KOKOSZKA,[1a] AND
GILBERT GORDON[1b]

Copper(II) acetate monohydrate is a binuclear complex.[2] At low temperatures it is diamagnetic and

(1) (a) National Bureau of Standards; (b) University of Maryland.

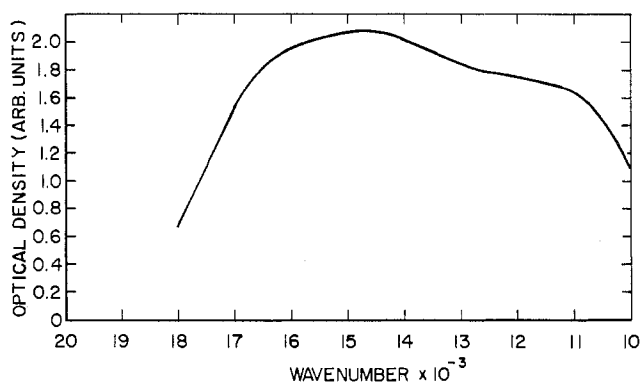(2) J. N. van Niekerk and F. R. L. Schoening, *Acta Cryst.*, **6**, 227 (1953).

Figure 1.—Unpolarized single crystal spectrum of copper acetate at 77°K. The peak at about 14,700 cm.$^{-1}$ has been instrumentally flattened relative to the 11,000 cm.$^{-1}$ peak.

at higher temperatures it is paramagnetic.[3] The electronic spectrum of this most interesting material has been investigated.[4,5] The polarization properties of two absorption bands, one at 14,400 cm.$^{-1}$ and the other at 27,000 cm.$^{-1}$, have been determined.[5] Our interest in re-investigating this spectrum arose when survey spectra revealed the presence of a previously unreported band in single crystals at approximately 11,000 cm.$^{-1}$. The new absorption band appeared as a shoulder on the 14,400 cm.$^{-1}$ band at room temperature but became quite pronounced at liquid nitrogen temperature (Figure 1). Graddon[6] has also observed a band at about 11,000 cm.$^{-1}$ in solutions containing dimeric copper(II) alkanoates.

The crystal spectra were taken on a Cary Model 14 spectrophotometer. Crystals were ground by hand to a thickness of approximately 0.2 mm., and the thickness was further reduced by etching with water. Spectroscopic measurements with polarized light were carried out on these crystals in the regions 8000–11,000 and 15,500–30,000 cm.$^{-1}$. Since the polarization properties of the 14,400 cm.$^{-1}$ band have been reported[4,5] and because of the large extinction coefficient in this region, this band was not studied in detail.

Measurements in the regions indicated above showed that the apparent band center[7] of the 11,000–14,400 cm.$^{-1}$ bands was sensitive to the direction of polarization of incident light. This indicates that the 11,000 and 14,400 cm.$^{-1}$ bands do not have the same polarization properties, since the apparent band center can change with the direction of incident polarized light only if the polarization directions of the 11,000 cm.$^{-1}$ band differ from that of the 14,400 cm.$^{-1}$ band. Measurements on the [110] face indicated that the apparent band center occurred closest to the 11,000 cm.$^{-1}$ band

(3) B. Bleaney and K. D. Bowers, *Phil. Mag.*, **43**, 372 (1952); H. Kumagai, H. Abe, and J. Shimada, *Phys. Rev.*, **87**, 385 (1952).

(4) S. Yamada, S. Nakamura, and R. Tsuchida, *Bull. Chem. Soc. Japan*, **30**, 953 (1957).

(5) M. L. Tonnet, S. Yamada, and I. G. Ross, *Trans. Faraday Soc.*, **60**, 840 (1964).

(6) D. P. Graddon, *J. Inorg. Nucl. Chem.*, **14**, 161 (1960); **17**, 222 (1961).

(7) We define the apparent band center as the bisector of lines which connect points of equal extinction coefficient in an extinction coefficient *vs.* energy plot where measurements are made in the wings of a band or band systems.

when the light was polarized along the direction in which the *z*-polarized 27,000 cm.$^{-1}$ band was maximized. Measurements on crystals polished perpendicular to the *b* axis revealed that the apparent band center again occurred closest to the 11,000 cm.$^{-1}$ band when the *z*-polarized 27,000 cm.$^{-1}$ band reached a maximum. Measurements on other crystal faces showed the same correlation between shift in apparent band center toward 11,000 cm.$^{-1}$ and the intensity of the 27,000 cm.$^{-1}$ band. Thus, we have concluded that the 11,000 cm.$^{-1}$ band is *z*-polarized.

With the assignment of the 11,000 cm.$^{-1}$ band as *z*-polarized it is noted that copper(II) acetate monohydrate has three absorption bands in the 8000–30,000 cm.$^{-1}$ region with the indicated polarizations: 11,000 cm.$^{-1}$ (*z*), 14,400 cm.$^{-1}$ (*x*, *y*), and 27,000 cm.$^{-1}$ (*z*). Recent magnetic measurements[8] indicate that the individual Cu(II) ions in dimeric copper(II) acetate monohydrate are only weakly coupled and that the energy levels can be described in terms of a single, six-coordinated cupric ion and the ground state in terms of the "hole" formalism can be described as essentially $d_{x^2-y^2}$.

With this choice of ground state, the polarizations of symmetry-allowed transitions based upon three possible choices of effective symmetry at a cupric ion can be summarized as is shown in Table I.

TABLE I

PREDICTED POLARIZATIONS FOR OPTICAL TRANSITIONS FOR COPPER ACETATE

Transition	C_{4v}	C_{2v}	C_2
$x^2 - y^2 \rightarrow z^2$	. . .	*z*	*z*
$x^2 - y^2 \rightarrow xy$	. . .	. . .	*z*
$x^2 - y^2 \rightarrow xz$	*xy*	*x*	*x*, *y*
$x^2 - y^2 \rightarrow yz$	*xy*	*y*	*x*, *y*

The observed spectrum can now be considered in terms of the requirements of these symmetry groups.

14,400 Cm.$^{-1}$ Band (*xy*-Polarized).—This band can be assigned to the $d_{x^2-y^2} \rightarrow d_{xz}$, d_{yz} transitions since these transitions are symmetry-allowed along *x* and *y* in C_{4v} and C_2 and along *x* and *y*, respectively, in C_{2v}. The shifts in peak position of this band with direction of polarization of incident light,[5] however, and the existence of two in-plane *g* values suggest a choice of symmetry lower than C_{4v}.

27,000 Cm.$^{-1}$ Band (*z*-Polarized).—The origin of this band *has not* been established but *if* it is a d–d band it can be assigned as the $d_{x^2-y^2} \rightarrow d_{z^2}$ transition, where presumably the stabilization of the d_{z^2} level of one cupric ion has occurred through the axial perturbation by the other cupric ion in the dimer. The $d_{x^2-y^2} \rightarrow d_{z^2}$ transition is symmetry-allowed along *z* in both groups, C_{2v} and C_2. Under the group C_{4v}, the vibronic mechanism must be invoked in order to account for the $d_{x^2-y^2} \rightarrow d_{z^2}$ transition.

11,000 Cm.$^{-1}$ Band (*z*-Polarized).—The $d_{x^2-y^2} \rightarrow d_{z^2}$ transition is symmetry-allowed along the *z* axis

(8) G. Kokoszka, H. C. Allen, Jr., and G. Gordon, *J. Chem. Phys.*, in press.

in C_{2v} and C_2 and vibronically-allowed along z in C_{4v}. The $d_{x^2-y^2} \rightarrow d_{xy}$ transition is allowed along z in C_2 symmetry and can only occur through vibronic coupling in C_{2v} and C_{4v}. Thus, if the $d_{x^2-y^2} \rightarrow d_{z^2}$ transition accounts for the 27,000 cm.$^{-1}$ band, the 11,000 cm.$^{-1}$ band can be assigned as the $d_{x^2-y^2} \rightarrow d_{xy}$ transition. If the 27,000 cm.$^{-1}$ band (which does seem high for a copper d–d transition) does not correspond to $d_{x^2-y^2} \rightarrow d_{z^2}$, then the 11,000 cm.$^{-1}$ band may correspond to either or both the $d_{x^2-y^2} \rightarrow d_{x^2}$ and the $d_{x^2-y^2} \rightarrow d_{xy}$ transitions.

Hansen and Ballhausen[9] have recently reviewed the theoretical aspects of this problem and have proposed a new interpretation of the electronic spectrum of copper(II) acetate monohydrate. References to previous theoretical work may be found in their paper.

(9) A. E. Hansen and C. J. Ballhausen, to be published.

An Extended Hückel Theory Investigation of the Electronic Structure of 2,4-Diiododecaborane(12), $B_{10}H_{12}I_2$

By Emmett B. Moore, Jr.

We have carried out an extended Hückel theory (EHT) molecular orbital (MO) investigation[1] of the electronic structure of $B_{10}H_{12}I_2$ in order to predict some of its physical properties, as has been done for $B_{10}H_{14}$ in similar studies,[2-4] and specifically to determine theoretically the polarizations of the first allowed electronic transitions in order to compare them with the experimental polarizations observed by Smallwood and Eberhardt.[5] For this purpose we have used Hoffmann's IBM 7094 EHT program.[4,6] This program computes molecular orbital coefficients and energies for up to 68 atomic orbitals given the atomic positions of up to 20 hydrogen atoms and up to 17 atoms of principal quantum number 2. The basis atomic orbitals are 1s Slater orbitals for hydrogen and 2s, $2p_x$, $2p_y$, and $2p_z$ Slater orbitals for the other atoms. The program computes all ss, sσ, $\sigma\sigma$, and $\pi\pi$ type overlap integrals and resolves them into appropriate integrals between basis orbitals. The program also allows one to use whatever values for the Slater ex-

(1) For a more complete discussion, see E. B. Moore, Jr., "The Electronic Structure of $B_{10}H_{12}I_2$," Boeing Scientific Research Laboratories Document D1-82-0352, March 1964.

(2) E. B. Moore, Jr., L. L. Lohr, Jr., and W. N. Lipscomb, *J. Chem. Phys.*, **35**, 1329 (1961).

(3) E. B. Moore, Jr., *ibid.*, **37**, 675 (1962).

(4) R. Hoffmann and W. N. Lipscomb, *ibid.*, **37**, 2872 (1962).

(5) E. Smallwood and W. H. Eberhardt, private communication.

(6) R. Hoffmann's extended Hückel theory computer program is available from the Quantum Chemistry Program Exchange, Chemistry Department, Indiana University, Bloomington, Ind.
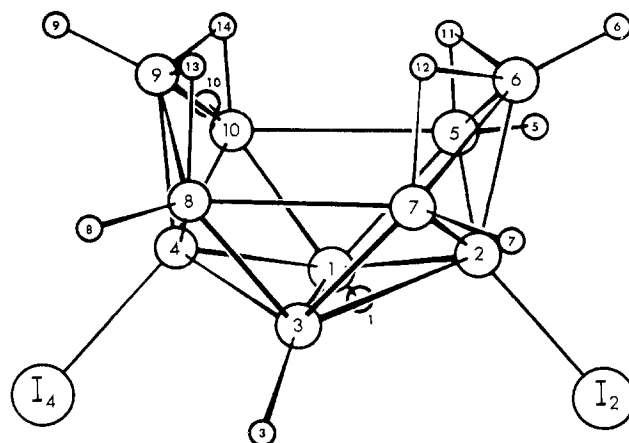

Figure 1.—$B_{10}H_{12}I_2$. The boron and hydrogen atoms are numbered conventionally and each iodine atom takes the number of its nearest neighbor boron atom. The twofold (z) axis is perpendicular to the line B-1–B-3.

ponents and Coulomb integrals one wishes and allows several choices for resonance integrals. We report here results for two alternate choices of the resonance integral: $H_{ij} = KS_{ij}$ with a value of -18.0 e.v. for K and $H_{ij} = 0.5K'(H_{ii} + H_{jj})S_{ij}$ with a value[7] of 1.75 for K'. The program also computes the population matrix and charge distribution in the molecule.

To obtain the positions of the atoms in $B_{10}H_{12}I_2$ we synthesized the $B_{10}H_{12}I_2$ results of Schaeffer[8] and the $B_{10}H_{14}$ results of Moore, Dickerson, and Lipscomb.[9] Synthesis is necessary because Schaeffer's X-ray work located only the iodine atoms with respect to the boron framework and not the boron atoms individually in the $B_{10}H_{12}I_2$ crystal. We forced the atomic positions into C_{2v} symmetry because the molecules have nearly this symmetry in the crystal, even though the space groups[8,10] require only C_2 symmetry. The structure of $B_{10}H_{12}I_2$ is derived from $B_{10}H_{14}$ by replacing hydrogen atoms 2 and 4 by iodine atoms (Figure 1).

For the hydrogen 1s, boron 2s and 2p, and iodine 5p Coulomb integrals we chose Mulliken's values[11] of the valence state ionization energies, which are -13.60, -15.36, -8.63, and -11.16 e.v., respectively. For the iodine 5s Coulomb integral we chose -21.09 e.v., which is consistent with Mulliken's other values. For the hydrogen and boron Slater exponents we used 1.0 and 1.3, respectively. Since the presently available EHT program does not handle atoms of principal quantum number 5, we varied the iodine Slater exponent and found that 1.3 gave values for the overlap integrals involving iodine orbitals which are good approximations to, but somewhat less than, the correct values.

Results

Our results are summarized in Table I for both $B_{10}H_{14}$ and $B_{10}H_{12}I_2$. Both molecules have stable, closed-

(7) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963).

(8) R. Schaeffer, *J. Am. Chem. Soc.*, **79**, 2726 (1957).

(9) E. B. Moore, Jr., R. E. Dickerson, and W. N. Lipscomb, *J. Chem. Phys.*, **27**, 209 (1957).

(10) J. S. Kasper, C. M. Lucht, and D. Harker, *Acta Cryst.*, **3**, 436 (1950).

(11) R. S. Mulliken, *J. Chem. Phys.*, **2**, 782 (1934).