AD-A038 090 HARVARD UNIV CAMBRIDGE MASS DEPT OF CHEMISTRY F/G 7/2
CRYSTAL AND MOLECULAR STRUCTURE.(U)
MAR 77 W N LIPSCOMB N00014-76-C-0199
UNCLASSIFIED NL

| OF |
ADA038090

END

DATE
FILMED
4-77

(12)
NW

FINAL REPORT

of research sponsored by

THE OFFICE OF NAVAL RESEARCH

Contract N00014-76-C-0199
NR 053-178

CRYSTAL AND MOLECULAR RESEARCH

William N. Lipscomb
Principal Investigator

Department of Chemistry
Harvard University
Cambridge, Massachusetts 02138

March 1977

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) (6) Crystal and Molecular Structure.		5. TYPE OF REPORT & PERIOD COVERED Final Report 4/1/68 - 1/31/77 ✓
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) (10) William N. Lipscomb, Principal ~~Investigator~~, and co-authors		8. CONTRACT OR GRANT NUMBER(s) (15) N00014-76-C-0199 new NR 053-178
9. PERFORMING ORGANIZATION NAME AND ADDRESS Harvard University, Dept. of Chemistry ✓ Cambridge, Massachusetts 02138		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Dept. of the Navy Arlington, Virginia 22217		(11) 12. REPORT DATE March 1977
		13. NUMBER OF PAGES 28
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) (9) Final rept. 1 Apr 68 - 31 Jan 77		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

(12) 31p.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

boranes, carboranes, three center bonds, molecular orbitals, molecular orbital methods for prediction, bonding, fractional multicenter bonds, chemical reactivity, molecular transformation

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The history of the early chemical and structural studies of boranes is referred to briefly with emphasis on the geometrical differences between compounds of carbon, and the more compact compounds of boron. The second part discusses the nature of three-center bonds, and their use in explaining the bonding in some of the more open types of boron compounds.

(continued)

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE S/N 0102-014-6601 |

Unclassified

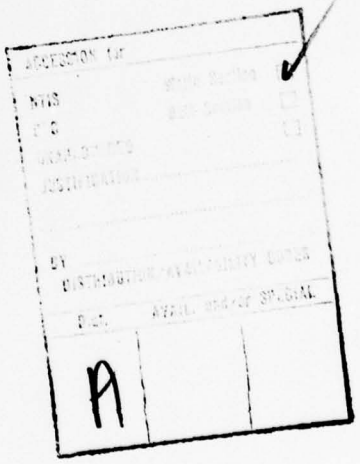
SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

163730

LB

20. continued

In the third part molecular orbitals are described, with special reference to their transferability among geometrically related systems. The use of molecular orbital methods for prediction is exemplified. This part is followed by a discussion of localized molecular orbitals, which produces an objective justification for the early use of three-center bonds, and describes the level of approximation for which three-center bonds are reasonably nearly correct. Further new types of bonds which are called fractional multicenter bonds are described within the framework of rigorous observation of the Pauli exclusion principle. Finally the value of all of these methods is tested for predictions of chemical reactivity and molecular transformations with emphasis on boranes and carboranes.



FINAL REPORT - ONR Contract N00014-76-C-0199

Professor William N. Lipscomb
Department of Chemistry, Harvard University

April 1, 1968 - January 31, 1977

Molecular SCF Calculations for SiH_4 and H_2S, F.P. Boer* and W.N. Lipscomb, J. Chem. Phys. 50, 989 (1969).

Wavefunctions and Hamiltonian matrices are obtained for SiH_4 and H_2S by the LCAO MO SCF method. Integrals were calculated accurately over minimum basis sets of Slater-type atomic orbitals, augmented by the addition of the 3d orbitals. Best atom exponents were used, except for the Hls, Si3d, and S3d orbitals, which were optimized to values SiH_4: Hls, 1.26; Si3d, 1.30, and H_2S: Hls, 1.22; S3d, 1.71. The calculated molecular energies are -290.5187 a.u. for SiH_4 and -397.8415 a.u. for H_2S, and net atomic charges are +0.127 for each hydrogen in SiH_4 and +0.176 for each hydrogen in H_2S.

* Dow Chemical Co.

Structures of $B_{20}H_{18}^{-2}$, $B_{20}H_{18}NO^{-3}$ and Conformations of the Triethylammonium Ion, C.H. Schwalbe and W.N. Lipscomb, J. Am. Chem. Soc. 91, 194 (1969).

Polyhedral $B_{10}H_{10}^{2-}$ is oxidized by Fe^{3+} to yield $B_{20}H_{18}^{2-}$, in which we have located H atoms, and by NO_2 to yield a product called $B_{14}H_{12}NO^{2-}$, but which we show here to be $B_{20}H_{18}NO^{3-}$. Solutions of the disordered crystal structures of the triethylammonium salts of these ions also yield six conformations of this positive ion and precise interatomic distances for the B_{10} units in the negative ions.

Rearrangements of Icosahedral Monohalo-m-carboranes, H.V. Hart and W.N. Lipscomb, J. Am. Chem. Soc. 91, 771 (1969).

Polyhedral rearrangements of 9-bromo-o-carborane at 395-425° yield all possible ortho and meta isomers, but yield no transformations of the meta isomers which are produced. Production of p-carborane from m-carborane at 500-620° raises questions concerning the mechanisms of further transformations and the equilibrium distributions of products at these higher temperatures. We report here the results of rearrangements of 9-chloro-m-,2-chloro-m-, 4-chloro-m-, 5-chloro-m-, chloro-p-, fluoro-p-2-fluoro-m-, and 4-fluoro-m-carboranes at 560-570°.

Molecular SCF Calculations for ScH_3NH_3 and TiH_3F, P.E. Stevenson and W.N. Lipscomb, J. Chem. Phys. 50, 3306 (1969).

Exact minimum Slater basis sets have yielded LCAO-MO-SCF wavefunctions for the model compounds ScH_3NH_3 and TiH_3F. The dative bond in ScH_3NH_3 has a small overlap population (0.11 electron) and a small charge transfer of only 0.12 electron from N into, primarily, $4p_z$ and $3d_z$ of Sc, but there are comparable redistributions among the orbitals of e symmetry as well. The charge on F in TiH_3F is -0.28e, and the Ti-F bond has overlap populations of 0.20e in bonding orbitals of a symmetry, and 0.18e in those of e symmetry. Changes on each H atom (attached to the metal) are -0.28e in ScH_3NH_3 and -0.30e in TiH_3F.

Localized Bonds in SCF Wavefunctions for Polyatomic Molecules. I. Diborane, E. Switkes, R.M. Stevens, and W.N. Lipscomb (Harvard University) and M.D. Newton (Mellon Institute), J. Chem. Phys. 51, 2085 (1969).

Molecular SCF orbitals of B_2H_6 have been computed from optimized minimum basis sets which employ isotropic or anisotropic atomic 2p orbitals. These SCF wavefunctions have been transformed to localized MO's which maximize the self-energy, $D = \Sigma_i(\phi_i\phi_i|\phi_i\phi_i)$. This objective procedure strongly supports the three-center bond for each BHB bridge. The resulting hybrids are $sp^{2.5}$, with $\angle H_i\text{-}B\text{-}H_i = 125^\circ$ and $\angle H_b\text{-}B\text{-}H_b = 93^\circ$ for terminal and bridge H's, respectively.

X-Ray Evidence for Bonding Electrons in Diborane, D.S. Jones and W.N. Lipscomb, J. Chem. Phys. 51, 3133 (1969).

The results of this study support the statement that a considerable portion of the observed x-ray B-H bond shortening is due to the inadequacies of the spherical-atom model. Stated alternatively, it may be concluded that x-ray data of the quality of the data used for this study do indeed contain the effects of bonding.

Theoretical Determination of the Magnetic Properties of Diatomic AlH, E.A. Laws, R.M. Stevens and W.N. Lipscomb, Chem. Phys. Letters 4, 159 (1969).

The magnetic susceptibility and nuclear magnetic shielding in diatomic AlG are calculated using the coupled Hartree-Fock theory. Because of the similarity in the ground state electronic structure of AlH and BH, experimental verification of the susceptibility of AlH to within a few ppm would be a strong indication that BH is paramagnetic, as previously predicted.

Electronic Structures for Energy-rich Phosphates, D.B. Boyd and W.N. Lipscomb, J. Theoret. Biol. 25, 403 (1969).

The extended Hückel theory is applied to adenosine-5'-di- and triphosphate, and to the related molecules of adenosine-5'-monophosphate, inorganic ortho-, pyro- and triphosphate, adenine, D-ribose and adenosine. Charge distributions calculated for these three-dimensional molecules suggest that opposing resonance and electrostatic repulsions can contribute to the high free energies of hydrolysis of the polyphosphates near pH 7. Eigenvalues from SCF calculations on small, related compounds are found to be useful as valence state ionization potentials. A procedure for obtaining total energies within the EH framework is described which approximates experimental values better than the sum of the orbital energies. The phosphorus 3d orbitals contribute significantly to the stability of the phosphates. The charges along the backbone of the condensed phosphates alternate in sign. Little interaction is found between the phosphate and base moieties of the nucleotides in folded conformations.

Time-Dependent Coupled Hartree-Fock Calculation of Some Optical Properties of H_2, I.R. Epstein and W.N. Lipscomb, Chem. Phys. Letters 4, 479 (1970).

The dynamic polarizability, refractive index and Verdet constant of H_2 are calculated using a fully coupled time-dependent Hartree-Fock variation-perturbation method. Preliminary results for the dynamic polarizabilities of other molecules are also given.

Polyatomic SCF Calculations Utilizing Anisotropic Basis Sets of Slater-type Orbitals, E. Switkes, R.M. Stevens, and W.N. Lipscomb, J. Chem. Phys. 51, 5229 (1969).

Fully optimized SCF wavefunctions using minimum Slater-type basis sets have been obtained for BH_3, NH_3, C_2H_2, C_2H_4, HCN, and H_2CO. Calculations employing anisotropic minimum basis sets are reported for the NH_3, H_2O, HCN, and H_2CO. The lower SCF energies of the calculations for anisotropic sets are primairly due to a reduction in electron-electron repulsion. Improvements in calculated dipole moments occur when independent p-orbital components are used to describe lone pairs and covalent bonds. A geometry-optimized calculation for H_2O is also reported.

Analysis of Diborane X-ray Diffraction Data Utilizing Structure Factors Calculated from Molecular Wave Functions, D.S. Jones and W.N. Lipscomb, Acta Cryst. A26, 196 (1970).

Crystal unit-cell structure factors for diborane, B_2H_6, have been calculated for four possible molecular geometries, using densities obtained from self-consistent field molecular wave functions. These structure factors were fitted for various B-H distances to the experimental X-ray data for B_2H_6 by varying the parameters of several thermal vibration models. B-H bond lengths so determined have values about 0.05 Å longer than those determined by the usual spherical atom analysis of the X-ray data. Consideration of additional factors, such as the X-ray B-H bond shortening due to rigid rotation of the molecules in the crystal, leads to the conclusion that the bond length correction given by this treatment accounts for about two-thirds of the observed discrepancy between X-ray and electron diffraction values for the B-H bond lengths in diborane.

Molecular SCF Calculations for GaF, GaH_3, GeH_4, AsH_3, and H_2Se, Philip E. Stevenson (Worcester Polytechnic Inst.) and W.N. Lipscomb, J. Chem. Phys. 52, 5343 (1970).

Exact minimum Slater basic sets have yielded LCAO-MO-SCF wavefunctions for the compounds GaF, GaH_3, GeH_4, AsH_3, and H_2Se. Chemical binding in these molecules is in accord with a very simple model of bond formation. Parameters for nonempirical molecular orbital (NEMO) calculations are computed from the Hamiltonian matrices of these molecules and from the previously published results on the model compounds ScH_3NH_3 and TiH_3F. A planar geometry of the unobserved GaH_3 is indicated by a NEMO calculation.

Localized Bonds in Self-Consistent-Field Wave Functions for Polyatomic Molecules. II. Boron Hydrides, E. Switkes, W.N. Lipscomb, and M.D. Newton (Carnegie Mellon University), J. Am. Chem. Soc. 92, 3847 (1970).

The minimum basis set self-consistent-field wave functions for B_4H_{10}, B_5H_9, and B_5H_{11} have been localized by an objective procedure in which the orbital self-energy $D = \Sigma_i (ii|ii)$ is maximized. The uniqueness of this procedure is discussed in terms of the second-order self-repulsion energy and initialization with a unitary transformation generated from random numbers. The B-H (terminal) bonds are quite localized and reasonably transferable. Likewise the B-H (bridge)-B orbitals are well localized and tend to give increased bonding toward a BH group rather than a BH_2 group when both are involved in the bond. The unique H atom attached to the apex of B_5H_{11} shows bonding properties intermediate between those of a bridge H and a terminal H. In B_4H_{10} there is a reasonably well-localized B-B single bond. Neither B_5H_9 nor B_5H_{11} shows open B-B-B bonds involving nonadjacent basal B atoms. Ambiguities in the B_5H_9 localization arise from the weak coupling of the boron framework orbitals to the self-repulsion energy, but B_5H_{11} shows two nicely localized central three-center B-B-B bonds in which the bonding density is somewhat displaced toward the direction between the apical and BH boron atoms.

Studies of Polyatomic Molecules Using Self-Consistent-Field Wave Functions. B_4H_{10}, B_5H_9, and B_5H_{11}, E. Switkes, I.R. Epstein, J.A. Tossell, R.M. Stevens, and W.N. Lipscomb, J. Am. Chem. Soc. 92, 3837 (1970).

SCF wave functions for B_4H_{10}, B_5H_9, and B_5H_{11} show (1) all atomic (Mulliken) charges are less than ± 0.1 e, (2) apex borons are more negative than other borons, (3) borons in BH_2 groups are more positive than borons in BH groups, (4) no simple correlation exists between one-center diagonal F-matrix elements and charge, (5) all terminal hydrogens are negative and all bridge hydrogens are positive, (6) most properties of the unique hydrogen in the symmetry plane of B_5H_{11} are intermediate between bridge and terminal hydrogens, (7) bridge hydrogens between BH and BH_2 groups are more strongly bonded toward the BH group, and (8) very low electron density directly between two B atoms exists if these borons are joined by a bridge hydrogen.

Comments on the Barrier to Internal Rotation in Ethane, I.R. Epstein and W.N. Lipscomb, J. Am. Chem. Soc. 92, 6094 (1970).

We find marked discrepancies in the various contributions to the barrier between two very similar calculations. Even more surprising is the fact that SCF calculations employing vastly different basis sets have all produced barriers ranging only from 2.5 to 3.6 kcal/mole. Thus, it seems that the only presently known near invariant in ethane barrier calculations is the height of the barrier itself. Further analysis is required to reveal other and more illuminating invariants which may be useful in any "explanation" of the source of the barrier in ethane. Consideration of the overlap (exclusion principle) repulsion between filled C-H bond orbitals may unveil one such invariant.

Localized Bonds in SCF Wavefunctions for Polyatomic Molecules. III. C-H and C-C Bonds, M.D. Newton (Carnegie-Mellon University) and E. Switkes and W.N. Lipscomb (Harvard), J. Chem. Phys. 53, 2645 (1970).

Localized molecular orbitals which minimize the exchange energy have been obtained for CH_4, C_2H_6, C_2H_4, C_2H_2, CH_3CCH, C_3H_6, HCN and H_2CO. These objectively determined orbitals correspond to the inner shells, lone pairs, and two-center bonds of classical bonding theory. In each case where double or triple bonds occur, the local orbitals correspond to equivalent bent bonds. The hybrids in the C-C bonds of cyclopropane form angles of 28° with the internuclear direction. The local orbitals are analyzed in terms of hybridization, polarity, bond moments, bond directions, and delocalization. Calculation of the curvature of the self-repulsion energy surface provides an indication of the uniqueness of the results. Sigma-pi separability and the sensitivity of the local orbitals to changes in basis set are also discussed.

Approximate Wave Functions for Carboranes Parametrized from Self-Consistent Field Model Calculations, T.F. Koetzle and W.N. Lipscomb, Inorg. Chem. 9, 2743 (1970).

Molecular orbitals have been obtained by a nonempirical method for carboranes in the series $B_nC_2H_{n+2}$, using parameters from minimum basis set SCF calculations for $B_4C_2H_6$. Molecular energies, ionization potentials, charge distributions, and dipole moments have been calculated, and certain predictions made concerning relative reactivities of B atoms within each of these molecules.

Self-Consistent-Field Wave Functions for 1,2-$B_4C_2H_6$ and 1,6-$B_4C_2H_6$, I.R. Epstein, T.F. Koetzle, R.M. Stevens, and W.N. Lipscomb, J. Am. Chem. Soc. 92, 7019 (1970).

SCF molecular orbital wave functions for the two isomers of $B_4C_2H_6$ have been obtained from a minimum basis set of Slater-type atomic orbitals. Ionization potentials of 9.90 and 9.25 eV are predicted, respectively, for the 1,2 and 1,6 isomers. The 1,6 isomer is computed to be more stable than the 1,2 isomer by about 15 kcal/mol. Charge densities are presented in certain sections of these isomers. In 1,2-$B_4C_2H_6$, atom B_3 (attached to two C atoms) is expected to be slightly less reactive toward electrophiles than atom B_4 (attached to one C atom). The calculated dipole moment of 2.95 D makes the carbon side of the 1,2-isomer positive, but the value is expected to be too large by about a factor of 2, because of the minimum basis set.

Molecular and Crystal Structure of Dimethyl-1,6-dicarba-closo-decaborane(10), T.F. Koetzle and W.N. Lipscomb, Inorganic Chem. 9, 2279 (1970).

A three-dimensional single-crystal X-ray diffraction study at -20 to -35° shows the molecule of dimethyl-1,6-dicarba-closo-decaborane(10), $B_8H_8C_2(CH_3)_2$, to have essentially C_s symmetry. The B_8C_2 unit is a bicapped square antiprism only slightly distorted from full D_{4d} symmetry. The charges on the B atoms, determined by LCAO-MO methods, become more positive in the order B8 (attached to no C atoms) <B10, B7, B9, B3, B4 (attached to one C) <B2,B5 (attached to two C atoms). The compound crystallizes in the orthorhombic space group Pbca with eight molecules in a cell of dimensions a = 11.36 ± 0.01, b = 11.81 ± 0.01, and c = 14.74 ± 0.01 Å. A density of 0.997 g/cm^3 was calculated from these cell dimensions. The 1615 X-ray reflections observed on film were refined to $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.084$.

Molecular Momentum Distributions and Compton Profiles. I. General Theory and Boron Hydrides, I.R. Epstein and W.N. Lipscomb, J. Chem. Phys. 53, 4418 (1970).

A method is described for the calculation of momentum distributions and Compton profiles of polyatomic molecules. Distributions, profiles and momentum expectation values are calculated for the boron hydrides B_2H_6, B_4H_{10}, B_5H_9, B_5H_{11}, and B_6H_{10}. Contour maps of total and difference densities in momentum space are presented for diborane. The results are analyzed in terms of localized orbitals. The analysis shows that traditional concepts of two- and three-center electron pair bonds may find great utility in interpreting momentum space distributions.

Crystal Structure of Tris(triethylammonium) μ-Nitrosobis(nonahydrodecaborate). The Structure of μ-Nitroso(nonahydrodecaborate)(3-), C.H. Schwalbe and W.N. Lipscomb, Inorganic Chem. 10, 160 (1971).

The $B_{20}H_{18}NO^{3-}$ anion, μ-nitrosobis(nonahydrodecaborate)(3-), consists of two $B_{10}H_9$ units each joined via an apical boron to the nitrogen atom of a bridging NO group. The approximate symmetry of this anion is C_{2v}. Some delocalization of electrons is suggested by the B-N bond distances of 1.51(3) and 1.46(3) Å and by the N-O distance of 1.28(2) Å. A two-fold disorder is present in one triethylammonium ion, which has an idealized nearly flat conformation of C_3 symmetry. The two ordered triethylammonium ions each differ from C_3 symmetry by rotation of one ethyl group about a C-N bond. The monoclinic space group is $P2_1/n$, and there are four formula weights in a unit cell having parameters a = 24.44 (4), b = 16.68 (3), c = 9.65 (2) Å, β = 97.0 (2)°, ρ_{obsd} = 0.99 (2) g cm^{-3}, and ρ_{calcd} = 0.972 (4) g cm^{-3}. Nearly complete refinement has yielded $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.14$ for the 4555 X-ray maxima. The crystals are intensely purple, and the two visible absorption maxima are shifted toward the red in less polar solvents.

Crystal Structure of Bis(triethylammonium)Octadecahydroicosaborate. The Structure of Octadecahydroicosaborate(2-), C.H. Schwalbe and W.N. Lipscomb, Inorganic Chem. 10, 151 (1971).

The centrosymmetric $B_{20}H_{18}^{2-}$ ion, octadecahydroicosaborate(2-), consists of two B_{10} units, very similar to that in $B_{10}H_{10}^{2-}$, linked by B···B interaction among one pair of adjacent apical and equatorial B atoms from each B_{10} unit. These interactions are interpreted as involving two localized three-center BBB bonds among these four B atoms. Location of all H atoms indicates that no hydrogen bridges are present. The triethylammonium ion has approximately C_3 symmetry. Two-fold positional disorder exists in all ions in the monoclinic crystal, which has symmetry $P2_1/a$, and two formula weights per unit cell having parameters a = 17.52(2), b = 7.60(1), c = 11.72(1) Å, and β = 109.7(2)°. The value of $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ is 0.10 for the 1874 X-ray diffraction maxima.

Hexaborane(10). Self-Consistent Field Wave Function, Localized Orbitals, and Relationships to Chemical Properties, I.R. Epstein, J.A. Tossell, E. Switkes, R.M. Stevens, and W.N. Lipscomb, Inorganic Chem. 10, 171 (1971).

A minimum basis set of Slater orbitals for B_6H_{10} yields an SCF wave function in which atomic charges are -0.02 (e) on B1 (apex), 0.07 on B2, 0.06 on B3,B6, and 0.04 on B4,B5. Net hydrogen charges are -0.07 on H1 (apex), -0.04 on H2, -0.04 on H3,H6, -0.09 on H4,H5, 0.03 on bridge H23,H26 and 0.02 on bridge H34,H56. Localized orbitals, obtained by maximizing $D = \Sigma(\phi_i\phi_i|\phi_i\phi_i)$, yield uniquely central three-center bonds B1-B3-Br and B1-B5-B6 and single bonds B1-B2 and B4-B5. The short B4-B5 bond is especially strongly localized. Asymmetry is predicted in the bridge H atom bonding and positions. Relationships of these results to probable chemical behavior of B_6H_{10} and to the isoelectronic carboranes and ions are discussed.

X-ray Studies of Bonding Electrons. Corrections for Bonds to Hydrogen upon Extension of the Basis Sets, T.A. Halgren, R.J. Anderson, D.S. Jones and W.N. Lipscomb, Chem. Phys. Letters 8, 547 (1971).

X-H bond distances (X = B.C) found from X-ray diffraction data are anomalously shortened when spherical atom densities are used in the analysis. Of this shortening, 0.05 Å is associated with spherical atoms versus a minimum basis set, and an additional 0.03 Å is associated with extension of this basis set.

Beryllium Borohydride Structure in the Solid Phase, D.S. Marynick and W.N. Lipscomb, J. Am. Chem. Soc. 93, 2322 (1971).

Both bent and linear structures for BBeB in $Be(BH_4)_2$ have been suggested, with a variety of arrangements for bonds toward hydrogen atoms. Indirect evidence from the crystallographic diffraction pattern led to the conclusion that the solid phase consisted of discrete molecules. Our solution of this structure from a single crystal establishes that the solid consists of helical polymers, having a chemical repeat and a crystallographic polymeric unit.

Magnetic Properties of AlH and N_2 from Coupled Hartree-Fock Theory, E.A. Laws, R.M. Stevens, and W.N. Lipscomb, J. Chem. Phys. 54, 4269 (1971).

The magnetic susceptibility and nuclear magnetic shielding in AlH and N_2 have been calculated using coupled Hartree-Fock theory. The perpendicular component of the AlH susceptibility tensor is predicted to be positive, i.e., paramagnetic. Thus, AlH becomes a second example, in addition to BH, of a gas-phase molecule which has a component which should exhibit the phenomenon of temperature independent paramagnetism. Results for N_2 yield a total susceptibility within 5% of the experimental value. Although the nitrogen nucleus is correctly predicted to be antishielded, the quantitative agreement of the shielding with experiment is not as good as has previously been obtained from coupled Hartree-Fock calculations on other diatomics.

Self-Consistent-Field Studies of the Electronic Structures of Cyclopropane and Benzene, R.M. Stevens, E. Switkes, E.A. Laws, and W.N. Lipscomb, J. Am. Chem. Soc. 93, 2603 (1971).

Accurate SCF wave functions employing optimized minimum basis sets of Slater-type orbitals are presented for cyclopropane and benzene. Atomization energies and ionization potentials are calculated and compared with experiment. The energies of the $1e_{1g} \rightarrow 1e_{2u}$ ($\pi \rightarrow \pi^*$) spectroscopic transitions in benzene are approximated using the $1e_{2u}$ virtual orbital. Calculations of the diamagnetic susceptibility of benzene yield an anisotropy of reasonable value. Plots of calculated electron density are used to illustrate the nature of bent bonding in cyclopropane and σ-π interpenetration in benzene.

Boron Hydride Valence Structures. A Topological Approach, I.R. Epstein and W.N. Lipscomb, Inorganic Chem. 10, 1921 (1971).

A topological approach to boron hydride three-center valence structures is presented. The method differs from earlier ones in that, on the basis of SCF-localized orbital results, open BBB bonds are excluded. Most of the boron frameworks for molecules, ions, and intermediates which are known or thought to be among the more stable species give rise to more allowed valence structures than do hypothetical topologies. A new, simpler topological computer program is described. Several charge distribution dependent weighting schemes for population analyses are considered. New structures are predicted, and use of the method in elucidating reaction pathways and more stable isomers is illustrated.

The Molecular and Crystal Structure of Tetramethylammonium 1,6,8-Trichloroheptahydro-closo-decaborate(2-), F.E. Scarbrough and W.N. Lipscomb, Inorganic Chem. 11, 369 (1972).

The anion of the formula $[N(CH_3)_4]_2[B_{10}H_7Cl_3]$, tetramethylammonium 1,6,8-trichloroheptahydro-closo-decaborate(2-), has C_{2v} symmetry, with the three chlorines attached to one apical boron and two opposite equatorial borons which are nearest the other apical boron. The B_{10} cage shows no large distortion from the D_{4d} symmetry. The molecular packing is monoclinic with eight molecules in a unit cell of dimensions a = 13.75, b = 18.01, c = 18.35 Å, and $\beta = 90.89^{\circ}$. The space group symmetry is $P2_1/n$. Direct methods-symbolic addition was used to phase initially 305 of 2270 independent, nonzero reflections which were subsequently refined to an R factor of 0.12.

Molecular Orbitals for Large Molecules. VI. Parameterized Self-Consistent-Field Theory for Transition Metal Compounds, J.A. Tossell and W.N. Lipscomb, J. Am. Chem. Soc. 94, 1505 (1972).

A new method is presented for nonempirical SCF-LCAO-MO calculations on molecules containing third row atoms. Diagonal Fock Hamiltonian (F) matrix elements (α's) are calculated from accurate one-electron integrals, and from two-electron integrals which are calculated accurately or are obtained from the Ruedenberg approximation. Finite overlap off-diagonal F-matrix elements are calculated using parameters obtained from model SCF calculations on chemically similar small molecules, and a new algorithm is presented for zero-overlap elements. α's for core orbitals are approximated by a simple formula requiring only one-center integrals, all electrons are included, and the self-consistent-field equations are solved. Results are compared with those from ab initio SCF calculations, among which are those reported here for a series of diatomic hydrides, oxides, and fluorides of the elements from Co to Ge. A molecular orbital calculation on the ground state of the hypothetical square-planar ion CuF_4^{2-} ($^2B_{1g}$) employing the above approximate method is presented and compared with previous calculations and with experimental results on related compounds.

Fractional Three-Center Bonds in Carboranes, D.S. Marynick and W.N. Lipscomb, J. Am. Chem. Soc. 94, 1748 (1972).

Localizations of molecular orbitals by successive unitary transformations of a randomized set of molecular orbitals in 4,5-$C_2B_4H_8$, 1,6-$C_2B_4H_6$, and 2,4-$C_2B_5H_7$ have yielded a total of five atoms, four borons, and one carbon, which show a consistent new kind of localization. In representing this situation we have used a dotted component of each central three-center bond when there appear to be five bonds to B or C including the external bond to hydrogen, at B_2 in $C_2B_4H_8$, at C_1, B_3, and B_4 in 1,6-$C_2B_4H_6$, and at B_3 in 2,4-$C_2B_5H_7$.

Recognition of these fractional three-center bonds allows unique, or symmetry equivalent, single valence structures to be drawn for at least these carboranes, in such a way that a common feature of bonding is preserved. These results, together with the uniquely localized bonds in the boron hydrides listed above, suggest that similar simplified bonding diagrams may emerge from more complex boranes, carboranes, carbonium-like compounds, and their metal derivatives.

Crystal Structure of Beryllium Borohydride, D.S. Marynick and W.N. Lipscomb, Inorganic Chem. 11, 820 (1972).

The crystal structure of $Be(BH_4)_2$ consists of a helical polymer of BH_4Be and BH_4 units. Within the BH_4Be unit the Be···B distance is 1.918 ± 0.004 Å, while each Be is linked to two remaining BH_4 units (and each BH_4 to two Be) at a Be···B distance of 2.001 ± 0.004 Å. Within the BH_4Be units there are two hydrogen bridges between B and Be, and in the helical polymer each B···Be contact has two hydrogen bridges. The hydrogen arrangement about Be is approximately a trigonal prism, but the H atoms are much closer to B (about 1.1 Å) than to Be (1.5-1.6 Å). The crystal structure is tetragonal, the space group is $I4_1cd$, with a = 13.62 ± 0.01 Å and b = 9.10 ± 0.01 Å. The disagreement factor is $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.04$ for the 276 distinct diffraction maxima. A self-consistent field wave function based upon a minimum Slater set of orbitals yields charges of about 0.6 on Be, -0.5 on B, and 0.04-0.09 on H atoms of the three types. Bonding from Be to BH_4 occurs equally directly from Be to B as compared with bonding through bridge hydrogen atoms.

Structural Ambiguity of the $B_{10}H_{14}^{2-}$ Ion, W.N. Lipscomb (Harvard), R.J. Wiersema and M.F. Hawthorne (University of California, Los Angeles), Inorganic Chem. 11, 651 (1972).

The structure of $B_{10}H_{14}^{2-}$, not previously established, has been assumed to be similar to that of $B_{10}H_{12}(NCCH_3)_2$, with which it is isoelectronic in the sense that the ligand CH_3CN is replaced by H^-. In this structure of 2632 topology there are BH_2 groups at B_6 and B_9 and hydrogen bridges between B_5 and and B_{10} and between B_7 and B_8. However, the hydrogen atom arrangement observed in $B_{10}H_{14}$ is also a possibility in a structure of 4450 topology having bridges B_5HB_6, B_6HB_7, B_8HB_9, and B_9HB_{10}. This ^{11}B nmr study resolves this structural ambiguity and suggests relative emphasis on three-center resonance as compared with uniform charge distribution as a preferred criterion for resolving structural ambiguity when steric and other factors are comparable.

Approximations to Self-Consistent Field Molecular Wavefunctions, T.A. Halgren and W.N. Lipscomb, Proc. Nat. Acad. Sci. U.S.A. 69, 652 (1972).

Unparameterized and parameterized versions are outlined of a new method for approximating self-consistent field wavefunctions from first principles at the minimum basis set level for complex molecules containing hydrogen and first-row atoms. The Hartree-Fock self-consistent field equations for closed-shell molecules are solved, retaining all one-electron integrals, and approximating the two-electron Coulomb integrals, hybrid integrals, and exchange integrals of the form $(i_Aj_A|i_Aj_A)$ and $(i_Aj_B|i_Aj_B)$ for centers A and B. A symmetrically orthogonalized basis set is used and rotational invariance is achieved by transformation to local axes that are unique for atoms in anisotropic environments. Parameterization based upon first-principle self-consistent field wavefunctions for a large number of molecules yields F-matrix elements to 0.007 atomic units (au), density matrix elements to 0.007 electrons, orbital populations and atomic charges to 0.01-0.02 electrons, orbital energies to 0.01 au, and total energies to 0.02 au (all standard deviations), in computational times only a few times larger than those required for complete neglect of differential overlap calculations.

One-Electron Properties of Ammonia Computed from Near-Hartree-Fock Wavefunctions, E.A. Laws, R.M. Stevens, and W.N. Lipscomb, J. Chem. Phys. 56, 2029 (1972).

One-electron properties of ammonia are computed using a near-Hartree-Fock basis set of Slater orbitals. The properties considered include diamagnetic shielding and susceptibility constants, dipole moment, and nuclear quadrupole coupling constants. The basis set dependence of these properties and the effects of vibrational distortions due to the NH_3 inversion motion are investigated. All computed properties are found to lie within 5% of experimental values.

Bonding in Boron Hydrides, W.N. Lipscomb, Pure and Applied Chem. 29, 493 (1972). Also published in "Boron Compounds," Symposium Editor: B. Stibr, Butterworths (London), 1972.

Unique preferred localized valence structures for B_2H_6, B_4H_{10}, B_5H_{11} and B_6H_{10} have been found from accurate self-consistent field wavefunctions by maximizing Coulomb repulsions of electron pairs within orbitals. Objective evidence has thus been obtained for two-center BH, three-center bridge BHB, two-center BB and central three-center BBB bonds, but not, as yet, for open three-center BBB bonds. Localization in B_5H_9 is ambiguous, as it is in organic molecules such as benzene. More thermodynamical stable isomers or plausible reaction pathways appear to have more resonance structures, and less reactive (or more plausible) structures or intermediates appear to have more nearly uniform charge distributions.

A Self-Consistent Field Study of Decaborane(14), E.A. Laws, R.M. Stevens and W.N. Lipscomb, J. Am. Chem. Soc. 94, 4467 (1972).

A self-consistent field wavefunction for decaborane(14), $B_{10}H_{14}$, has been obtained from a minimum basis set of Slater-type orbitals. Electron density and difference density maps are used to discuss molecular bonding properties and possible valence structures. Static reactivity indices are found to correlate well with the experimental order of electrophilic and nucleophilic substitutions. The atomization energy and ionization potential are found in good agreement with experimental numbers, but the dipole moment is too large by roughly 40%. Theoretical values for the diamagnetic susceptibility and shielding constants are reported and the implications of these numbers discussed.

A Comparison of Diborane Molecular Properties from Minimum Basis Set and Extended Slater Orbital Wave Functions, E.A. Laws, R.M. Stevens and W.N. Lipscomb, J. Am. Chem. Soc. 94, 4461 (1972).

A comparison of extended and optimized minimum STO basis set wave functions for B_2H_6 indicates that boron hydride energies, ionization potentials, diamagnetic susceptibility and shielding constants, and total electron densities may be reliably determined from a minimum basis set calculation. Minimum basis set difference densities and nuclear quadrupole coupling constants are only qualitatively correct. Minimum basis set atomization energies appear to be more accurate than those computed with large basis sets, when the atomic wave functions are determined using the molecular exponents.

Aspects of the Electron Density Problem, Experimental and Theoretical, W.N. Lipscomb, Transactions of the American Crystallographic Association 8, 79 (1972).

Anomalous shortening of BH distances (and by inference CH, NH, ..., distances) when spherical atoms are used in X-ray refinements are largely due to effects of electron displacements into the chemical bonding region. A minimum atomic basis set accounts for 0.05 Å, while an extended basis set adds 0.03 Å more, when an accurate molecular wavefunction is substituted for spherical atoms. Difference electron densities are very sensitive to the atomic basis set used in computing a molecular wavefunction. In particular, a minimum basis set of atomic orbitals is inadequate. Difference densities are also sensitive to the choice of promotion and exponents of the atoms which are subtracted, and hence these atomic wavefunctions should be completely specified.

A Comparison of Minimum and Expanded Slater Basis Set Difference Density Maps, E.A. Laws and W.N. Lipscomb, Israel Journal of Chem. 10, 77 (1972)

A comparison of minimum and expanded Slater basis set difference densities in H_2, N_2 and $B2H_6$ indicates that minimum basis set results significantly underestimate the transfer and concentration of charge in molecular bonding regions.

Self-Consistent Field Wave Function and Localized Orbitals for 2,4-Dicarbaheptaborane(7). The Fractional Three-Center Bond, D.S. Marynick and W.N. Lipscomb, J. Am. Chem. Soc. 94, 8692 (1972).

A minimum basis set self-consistent field wave function for 2,4-dicarbaheptaborane(7) has been calculated. Molecular properties such as charge distributions, bond strengths, dipole moments, diamagnetic chemical shifts, ionization potentials, and atomization energy are examined and the reactivity of the molecule is discussed in terms of the ground-state charge distribution. Localized orbitals obtained by maximizing the self-repulsion energy yield one boron atom (B_3) which appears to be participating in five bonds to other atoms; however only fractions of atomic orbitals are used for some or all of these bonds. These fractional bonds are discussed in terms of their directional character, hybridization, and per cent delocalization, and the relationships among fractional bonding, molecular symmetry, and the topological theory of the boron hydrides are explored.

A Self-Consistent Field and Localized Orbital Study of 4,5-Dicarbahexaborane(8), D.S. Marynick and W.N. Lipscomb, J. Am. Chem. Soc. 94, 8699 (1972).

A self-consistent field wave function has been calculated for 4,5-dicarbahexaborane(8) using the experimental geometry and a minimum basis set of Slater orbitals. The charge distribution, reactivity, diamagnetic chemical shifts, ionization potential, atomization energies, and dipole moments are discussed in terms of the ground-state charge distribution. Localized orbitals are found by the Edmiston-Ruedenberg method and a modified Taylor method, and the valence structure of the molecule is described in terms of fractional three-center bonds. A detailed discussion of the nature of the extremum in the self-repulsion energy surface is presented. The relationship between the topological theory of the boron hydrides and the valence structure of the molecule is discussed.

Ab Initio Self-Consistent Field Calculation of the Energies of Formation of B_2H_6 and $B_2H_7^-$, J.H. Hall, Jr., D.S. Marynick, and W.N. Lipscomb, Inorganic Chem. 11, 3126 (1972).

The near Hartree-Fock limit for the ΔE of the reaction $2BH_3(g) \rightarrow B_2H_6(g)$ is found to be -19.0 kcal/mole, using a very large Slater orbital basis set. The ΔE for the reaction $BH_4^-(g) + BH_3(g) \rightarrow B_2H_7^-(g)$ is estimated to be -25.1 kcal/mole, using optimized minimum basis sets. The B-H-B three-centered bond in $B_2H_7^-$ is predicted to be linear and symmetric in the gas phase.

Localized Molecular Orbitals for 1,2- and 1,6-Dicarbahexaborane(6). The Open Three-Center Bond and Implications for Carborane Topology, I.R. Epstein, D.S. Marynick and W.N. Lipscomb, J. Am. Chem. Soc. 95, 1760 (1973).

Localized molecular orbitals (LMO's) have been calculated for the 1,2 and 1,6 isomers of $C_2B_4H_6$ by the Edmiston-Ruedenberg procedure. The 1,2 isomer is the first example found in LMO calculations of the existence of the open three-center bond, and it occurs here only for the BCB nuclear configuration. The LMO structure for the 1,6 isomer is best interpreted in terms of fractional three-center bonding. We discuss the implications of these results for the general application of topological methods to boranes and carboranes.

Self-Consistent-Field Wavefunctions for Complex Molecules. The Approximation of Partial Retention of Diatomic Differential Overlap, T.A. Hlagren and W.N. Lipscomb, J. Chem. Phys. 58, 1569 (1973).

A new approach, based on partial retention of diatomic differential overlap over an orthogonalized basis, is described for approximating LCAO SCF molecular orbital wavefunctions at the minimum basis set level for closed-shell molecules containing hydrogen and first-row atoms. The SCF equations are solved explicitly, retaining all one-electron integrals and approximating two-electron Coulomb integrals, hybrid integrals, and exchange integrals of the forms $(i_Aj_A|i_Aj_A)$ and $(i_Aj_B|i_Aj_B)$ for centers A and B. Single center averaging processes otherwise required for rotational invariance are avoided by the use of local atomic centered axes which are unique in anisotropic environments. The result is accuracy comparable to that of much more elaborate methods such as STO-3G, in computing times only moderately longer than for simpler methods based on neglect of differential overlap such as CNDO and INDO. Both unparameterized and parameterized methods are reported. Comparison of parameterized results with ab initio SCF results for a large number of molecules indicates that F-matrix elements are given to standard deviations of 0.007 a.u., density matrix elements to 0.007 electrons, orbital populations and atomic charges to 0.01 or 0.02 electrons, orbital energies to 0.01 a.u., and total energies to 0.03 a.u. Optimal geometries and computed force constants also agree well with reference SCF results. Computing times in seconds for the IBM 360/91 are $0.2+0.006N^2+0.00015N^3+0.0000012N^4$ for molecules with minimum basis sets of 2-64 atomic orbitals (N).

Crystal Structure of Tetramethylammonium Tetradecahydrodecaborate. Structure of the $B_{10}H_{14}^{2-}$ Ion, D.S. Kendall and W.N. Lipscomb, Inorganic Chem. 12, 546 (1973).

The $B_{10}H_{14}^{2-}$ ion has two BH_2 groups and two bridging hydrogen atoms, in a 2632 topology of three-center bond theory. The isolated ion has C_{2v} symmetry. Unit cell parameters of tetramethylammonium tetradecahydrodecaborate, $(N(CH_3)_4)_2B_{10}H_{14}$, are a = 9.60(1) Å, b = 16.29(1) Å, c = 12.27(1) Å, β = 91.63(1)°, and z = 4, and the crystal symmetry is $P2_1/c$. Full-matrix least-squares refinement of the structure yields a value of $R = \Sigma||F_o|-|F_c||/\Sigma|F_c|$ of 0.085 for 2058 X-ray diffraction maxima measured on a four-circle diffractometer. The relationships of the structure of $B_{10}H_{14}^{2-}$ to its bonding and probable reactivity are discussed briefly.

Optimized Self-Consistent-Field and Localized Molecular Orbital Studies of Tetraborane(4), J.H. Hall, Jr., I.R. Epstein and W.N. Lipscomb, Inorganic Chem. 12, 915 (1973).

The wave function for B_4H_4 has been computed in the SCF-LCAO-MO approximation. Slater-type orbital exponents and the boron-boron distance have been optimized. The calculation shows that B_4H_4 should be stable by 316.9 kcal/mole with respect to dissociation to form BH units. The Mulliken charges are +0.0046 e on the borons and -0.0046 on the hydrogens. Calculation of localized molecular orbitals for B_4H_4 using the *ab initio* Edmiston-Ruedenberg procedure yields four central three-center B-B-B bonds localized in the faces of the tetrahedron. These bonds are, surprisingly, nonsymmetric and unequivalent. Possible reasons for this result and for the apparent instability of B_4H_4 are discussed.

Localized Orbitals in Ethyl Ion and the Perturbation of Ethylene by a Proton. Reaction of Localized Orbitals, D.A. Dixon and W.N. Lipscomb, J. Am. Chem. Soc. 95, 2853 (1973).

As a proton approaches along the perpendicular bisector of the C-C line and normal to the plane of ethylene, appreciable orbital perturbations begin at 3.7 Å. Results at the self-consistent field level have been found for a minimum basis set of Slater orbitals using previously obtained equilibrium geometries for both the bridge (C_{2v}) and open ($CH_2CH_3^+$,C_s) structures. Localized orbitals have been obtained by maximizing the self-repulsion energy $\Sigma_i(ii|ii)$ and have been related to the formation of $C_2H_5^+$ from C_2H_4 and a proton, and to the subsequent addition of a nucleophile in the Markovnikov reaction.

Fluxional Behavior of $B_{11}H_{11}^{2-}$, E.I. Tolpin and W.N. Lipscomb, J. Am. Chem. Soc. 95, 2384 (1973).

Isomerization of $B_nH_n^{2-}$ ions is generally believed to be a high-temperature phenomenon. We report here the spontaneous isomerization of $B_{11}H_{11}^{2-}$ ions in solutions at low temperatures in nmr time scales.

Crystal and Molecular Structure of $[Me_4N]^+[PhCHB_{10}H_{10}CPh]^-$: Relation to the $C_2B_{10}H_{13}^-$ Ion, E.I. Tolpin and W.N. Lipscomb, J. Chem. Soc. Chem. Comm., p. 257 (1973).

A single-crystal X-ray diffraction study of $[Me_4N]^+$ $[PhCHB_{10}H_{10}CPh]^-$ shows a unique bridging C atom of the PhCH group on the face of an icosahedral ($B_{10}C$) fragment; there are no bridge hydrogens.

Thermal Rearrangements of Icosahedral Carboranes. Molecular and Crystal Structure of 5,15-Dichloro-1,7-dimethyl-1,7-dicarba-closo-dodecaborane(12), H.V. Hart and W.N. Lipscomb, Inorganic Chem. 12, 2644 (1973).

Thermal rearrangement of 9,12-dichloro-C,C'-dimethyl-o-carborane at 420° yields 5,15-dichloro-C,C'-dimethyl-m-carborane as the major product, in addition to a large number of the possible 15 other meta isomers. This major product is the only one expected from the cuboctahedral intermediate mechanism. Other products may result from triangle rotations in this intermediate and possibly from other less important mechanisms. This major product is orthorhombic, in the space group $Pmn2_1$, and has two molecules in a unit cell having dimensions of a = 7.725, b = 10.181, and c = 8.079 Å. The value of $R_F = \Sigma||kF_o| - |F_c||/\Sigma|kF_o|$ is 0.078 for 460 observed diffraction maxima.

Ab Initio Self-Consistent Field and Configuration Interaction Study of Beryllium Borohydride, D.S. Marynick and W.N. Lipscomb, J. Am. Chem. Soc. 95, 7244 (1973).

Optimized geometries and relative energies are reported for many possible structures of beryllium borohydride. These calculations are at the ab initio minimum basis set self-consistent field level of approximation, with near optimum exponents. Configuration interaction calculations on the bound conformers with all valence shell single and double excitations included suggest that two or three conformers may coexist in the gas phase. This result is also based on the available experimental evidence. The previous experimental work on the gas phase is discussed in view of the above possibility.

Three-Center Bonds in Electron-Deficient Compounds. The Localized Molecular Orbital Approach, W.N. Lipscomb, Accts. of Chem. Res. 6, 257 (1973).

Summary:

(a) No open three-center bonds have been found in localized molecular orbitals of boranes.

(b) Carboranes, but not boranes, may have open three-center bonds, where C is the central atom, and may have an adjacent pair of C atoms (or an adjacent B and C) joined by both a single bond and a central three-center bond.

(c) Unique preferred three-center bonds exist in valence structures of B_2H_6, B_4H_{10}, B_5H_{11}, B_6H_{10}, and 1,2-$C_2B_4H_6$.

(d) Structures for which 3-center bonds can be drawn are preferred over those which cannot be so expressed. For example, $B_{11}H_{11}^{2-}$ of C_{2v} symmetry is preferred over the C_{5v} structure.

(e) Of alternative geometries for an isomer, the structure having the larger number of nearly equivalent three-center bond structures is preferred. This argument takes precedence over which choice has the more favorable charge distribution.

(f) Unique fractional three-center bond descriptions exist for 4,5-$C_2B_4H_8$ and probably also for $B_{10}H_{14}$, $B_{10}H_{14}^{2-}$, and $B_9H_{13}L$.

(g) Fractional three-center bonds occur replacing an open three-center bond and a single bond from the central atom to a fourth atom, except when C is the central atom.

(h) It is probable that valence structures having a vacant orbital which can easily be incorporated into three-center bond structures are preferred over those which cannot.

Crystal and Molecular Structure of Tetramethylammonium C,C'-Diphenyl-undecahydrodicarba-nido-dodecaborate(1-), E.I. Tolpin and W.N. Lipscomb, Inorganic Chem. 12, 2257 (1973).

The anion of the salt $(Me_4N^+)(PhCHB_{10}H_{10}CPh^-)$, tetramethyl-ammonium C,C'-diphenylundecahydrodicarba-nido-dodecaborate(1-), is an opened icosahedron. Except for the orientation of phenyl rings, this ion has C_s symmetry. One carbon is in the $B_{10}C$ icosa-hedral fragment, while the second carbon bridges two boron atoms in the open face of this fragment. This second carbon is also bonded to H and to a phenyl group. The unit cell contains four formula weights in the orthorhombic space group $P2_12_12_1$. Unit cell dimensions are a = 15.983(10) Å, b = 11.158(5) Å, and c = 12.941(3) Å. The final value of $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$ is is 0.093 for 1544 observed X-ray diffraction maxima.

Molecular Structure and Two Crystal Structures of 6-Isothiocyanodecaborane, 6-$B_{10}H_{13}NCS$, D.S. Kendall and W.N. Lipscomb, Inorganic Chem. 12, 2915 (1973).

The reaction of mercuric thiocyanate with 6,9-$B_{10}H_{12}(SMe_2)_2$ or 6,9-$B_{10}H_{12}(SEt_2)_2$ yields $B_{10}H_{12}NCS$. A new preparation from NaNCS and decaborane is described. X-ray structure determinations prove that the NCS group is attached covalently at the N atom to B6 of decaborane. The B-N bond is 1.435 Å in length, too short for a pure single bond. Identical molecular structures of $B_{10}H_{13}NCS$ have been found in two crystal structures, both in space group $P2_1/n$ with four molecules per unit cell. The form found at 13° has unit cell parameters a = 7.352(5), b = 14.611 (5), c = 10.561(5) Å, and β = 105.273 (13)°. Full-matrix, least-squares refinement gives $R = \Sigma||F_o|-|F_c||/\Sigma|F_o| = 0.063$ for 1181 X-ray diffraction maxima measured on a Picker four-circle diffractometer. Crystals grown at room temperature had unit cell parameters of a = 7.93 (1), b = 17.48 (1), c = 9.47 (1) Å, and β = 101.68 (2)°. Full-matrix, least squares refinement gives R = 0.087 for 716 reflections.

Crystal and Molecular Structure of Ammonia-Isothiocyanoborane, $NH_3 \cdot BH_2NCS$, D.S. Kendall and W.N. Lipscomb, Inorganic Chem. 12, 2920 (1973).

The crystal and molecular structure of $NH_3 \cdot BH_2NCS$, ammonia-isothiocyanoborane, has been determined. Distances from boron to nitrogen are 1.534 (8) Å to the NCS group and 1.578 (8) Å to the NH_3 unit. Unit cell distances are a = 9.250 (1), b = 6.781 (1), and c = 7.152 (1) Å. The space group is Pnma, and there are four molecules in the unit cell. Full-matrix least-squares refinement has yielded a value of $R = \Sigma||F_o|-|F_c||/\Sigma|F_o| = 0.043$ for 324 X-ray diffraction maxima measured on a Picker four-circle diffractometer. Comments are given on the relationship of this compound to other isothiocyanoboranes.

Self-Consistent Field Wave Functions of Boron Hydrides and Ions: B_8H_{12}, B_9H_{15}, $B_6H_6^{2-}$, $B_{10}H_{10}^{2-}$, and $B_{10}H_{14}^{2-}$, J.H. Hall, Jr., D.S. Marynick and W.N. Lipscomb, J. Am. Chem. Soc. 96, 770 (1974).

A minimum basis set of Slater orbitals has been used for *ab initio* self-consistent field wave functions for B_8H_{12}, B_9H_{15}, $B_6H_6^{2-}$, $B_{10}H_{10}^{2-}$, and $B_{10}H_{14}^{2-}$. From these wave functions we give bond midpoint densities, overlap populations, atomic charges, molecular dipole moments, diamagnetic susceptibilities, and diamagnetic shielding constants. Some analysis is also given relating probable sites of nucleophilic and electrophilic attack to the charge distributions, and some discussion is included relating to the few positive (unbound) occupied eigenvalues of the negative ions. A comparison is also made of these accurately computed SCF results with approximate SCF wave functions obtained by the method of partial retention of diatomic differential overlap (PRDDO). Excellent charge distributions and eigenvalues are obtained by the PRDDO method in computing times less than those of the SCF method by about a factor of 50.

Localized Molecular Orbitals and Chemical Reactions. II. A Study of Three-Center Bond Formation in the Borane-Diborane Reaction, D.A. Dixon, I.M. Pepperberg and W.N. Lipscomb, J. Am. Chem. Soc. 96, 1325 (1974).

Comparison of the symmetric (C_{2A}) approach of two BH_3 molecules to form B_2H_6 with the unsymmetric (C_s) approach in which only a single hydrogen bridge is formed leads to strong preference for the C_{2h} transition state having two very unsymmetrical hydrogen bridges. This symmetric state lies 2.6 kcal/mole of B_2H_6 higher than $2BH_3$ in a self-consistent field calculation extended by inclusion of all 14 single and 210 double excitations from the valence shells of a minimum Slater basis. The two equivalent unsymmetrical bridges have a long B···H interaction with a B-B distance of 3.0 Å in the transition state. The formation of the three-center BH_bB bond is investigated by examining the properties of the localized molecular orbitals along the symmetric pathway. A covalent three-center (bent) B-H···B forms as the B···B distance closes to about 2.1 Å, corresponding to a H···B distance of 1.65 Å.

Ab Initio Self-Consistent-Field Study of Boron Halides: B_4F_4 and B_4Cl_4, J.H. Hall, Jr. and W.N. Lipscomb, Inorganic Chem. 13, 710 (1974).

The molecules B_4F_4 and B_4Cl_4 have been studied by ab initio self-consistent-field (SCF) methods employing a minimum basis set of Slater orbitals. Mulliken overlap populations, atomic charges, midpoint densities, atomization energies, orbital populations, and ionization potentials are reported, and some quantities are compared to earlier results on B_4H_4. The MO's for B_4F_4 and B_4Cl_4 consist of E, T_1, and T_2 bonding orbitals composed mainly of fluorine 2p and chlorine 3p orbitals. Thus, both molecules are stabilized by back donation of ligand p orbitals into the B_4 tetrahedron. The antibonding E*, T_1*, and T_2* MO's are composed mostly of boron 2p orbitals. The amount of ligand π back-donation into the B_4 tetrahedron is greater for B_4F_4 than for B_4Cl_4. Localized molecular orbitals for B_4F_4 and B_4H_4 are obtained by using Boys' method of maximizing the sum of the squares of the distances between the orbital centroids, and the results for B_4H_4 are compared to our earlier Edmiston-Ruedenberg localization results for B_4H_4.

Localized Molecular Orbital Description of Nitrogen Lone Pairs, D.A. Kleier, J.H. Hall, Jr., T.A. Halgren, and W.N. Lipscomb, Proc. Nat. Acad. Sci. U.S. 71, 2265 (1974).

The Boys localization procedure is applied to several molecules possessing nitrogen lone pairs. The Boys structures show a tendency for the N lone pairs to participate in bonding to nearby electron sinks. For example, the Boys structure for planar formamide has two equivalent τ-bond orbitals between the carbonyl carbon and nitrogen atoms. The change in this description with variation of geometry at nitrogen is treated, and analogous Edmiston-Ruedenberg localizations on formamide are included for comparison.

Comment on Crystal Structures of α-CO and α-N_2, W.N. Lipscomb, J. Chem. Phys. 60, 5138 (1974).

Crystalline α-CO, known to have a residual entropy of almost Rln2 (experimental value, 1.1±0.1 cal·deg^{-1}·mole^{-1}) has recently been assigned a disordered structure (CO or OC) in the space group Pa3. Molecular centers for the four molecules in the cubic unit cell are at 000, $\frac{1}{2}0\frac{1}{2}$, $0\frac{1}{2}\frac{1}{2}$, and $\frac{1}{2}\frac{1}{2}0$, and molecular axes are aligned parallel to the cell diagonals. These authors reject the space group $P2_13$ of lower symmetry, in which displacement of the molecular center is possible along the directions of cell diagonals, on the basis that it is "characterized by the ordered arrangement of the ends of the molecules along the body diagonals." They therefore suggest that the $P2_13$ crystal structure is in conflict with the disorder required by the residual entropy. We wish to comment that a disordered structure for CO is possible in the space group $P2_13$, and that no contradiction need exist between the residual entropy and the choice of $P2_13$ as the space group.

Localized Molecular Orbital Description of Nitrogen Lone Pairs, D.A. Kleier, J.H. Hall, Jr., T.A. Halgren and W.N. Lipscomb, Proc. Nat. Acad. Sci. USA, 71, 2265 (1974).

The Boys localization procedure is applied to several molecules possessing nitrogen lone pairs. The Boys structures show a tendency for the N lone pairs to participate in bonding to nearby electron sinks. For example, the Boys structure for planar formamide has two equivalent π-bond orbitals between the carbonyl carbon and nitrogen atoms. The change in this description with variation of geometry at nitrogen is treated, and analogous Edmiston-Ruedenberg localizations on formamide are included for comparison.

Localized Orbitals in Large Boron Hydrides. Hexadecaborane and Related Molecules, D.A. Dixon, D.A. Kleier, T.A. Halgren, and W.N. Lipscomb, J. Am. Chem. Soc. 96, 2293 (1974).

Localized MO's (LMO's) were obtained for $B_{16}H_{20}$ by using the method of S.F. Boys (1966) with partial-retention-of-diatomic-differential-overlap wave functions (Halgren and Lipscomb, 1973). The LMO's of the $B_{10}H_{14}$-like region and the B_8H_{12}-like region are similar to the LMO's in $B_{10}H_{14}$ and B_8H_{12}. The difference between the LMO's in the $B_{10}H_{14}$-like region of $B_{16}H_{20}$ and those of $B_{10}H_{14}$ is attributed to differences in charge distributions. The fractional bonding found in $B_{16}H_{20}$ is explained in terms of donation of charge from electron-rich to electron-poor regions.

Boron Hydride Derivatives for Neutron Capture Therapy. Antibody Approach, H.S. Wong, E. I. Tolpin and W.N. Lipscomb, J. Med. Chem. 17, 785 (1974).

A number of borane derivatives which have potential use in binding to proteins for neutron capture therapy have been synthesized from orthocarborane ($C_2B_{10}H_{12}$) and from decahydrocecaborate(2-). These modifying reagents contain either amine, imido ester, or aldehyde functions and are solubilized by ionic centers. Additional derivative chemistry of orthocarborane is reported. In particular, a six-membered ring amide carborane synthesized here is shown to resist hydrolysis under drastic acidic conditions.

Binding Studies of Boron Hydride Derivatives to Proteins for Neutron Capture Therapy, E.I. Tolpin, H.S. Wong and W.N. Lipscomb, J. Med. Chem. 17, 792 (1974).

Ionically solubilized boron hydride derivatives previously reported by us, including diazonium ions, imido esters, aldehyde, and amines, are used to bind boron to human -globulin and bovine serum albumin. The results indicate that an average of 0.6% boron by weight can be attached to the antibody at 50% precipitation of the original protein and a maximum of 0.8% boron by weight near quantitative precipitation as determined by extrapolation. An isocyanate derivative of the $B_{10}H_{10}^{2-}$ anion gives up to 1.77% by weight of boron bound without significant loss of protein solubility.

Localized Orbitals in Boron Fluorides. Highly Polarized Boron-Fluorine Double and Triple Bonds, J.H. Hall, Jr., T.A. Halgren, D.A. Kleier and W.N. Lipscomb, Inorganic Chem. 13, 2520 (1974).

A localized molecular orbital (LMO) description is presented for the valence structures for the boron fluorides BF, BH_2F, BF_2H, BH_3, BF_2NH_2, B_4F_4, and B_2F_4. The highly polar equivalent BF triple bonds in B_4F_4 and BF double bonds in BH_2F, BF_2H, BF_3, BF_2NF_2, and B_2F_4 are described. The equivalent double and triple bonds obtained for these polyatomic molecules differ in important ways from the conventional description of a single B-F bond having some back-donation to the π system. First, all components of a multiple bond in a given BF interaction are equivalent. Second, all components are highly polar, having an excess of electrons on F and leaving atoms neutral within about 0.1-0.2 electron of charge. Finally, these multiple bonds are unexpected in the sense that they have not been described previously for BF bonds in polyatomic molecules from conventional valence-bond theory.

Localized Molecular Orbitals for Polyatomic Molecules. I. A Comparison of the Edmiston-Ruedenberg and Boys Localization Methods, D.A. Kleier, T.A. Halgren, J.H. Hall, Jr. and W.N. Lipscomb, J. Chem. Phys. 61, 3905 (1974).

The Edmiston-Ruedenberg (ER) and Boys localization methods are compared for a number of boron hydrides and carboranes. The Boys localization equations are solved explicitly for the two-orbital case and an iterative procedure for the multidimensional case is presented. The Boys analogs of Taylor's [J. Chem. Phys. 48, 2385 (1968)] ER equations are derived and the second-order term is converted into a symmetrized quadratic form which is analogous to the ER equations of Switkes et al. [J. Am. Chem. Soc. 92, 3847 (1970)]. A limited second-derivative test is employed in order to determine the nature of the convergence, and a transformation based on it is defined which successfully resolves structural ambiguities to which the standard two-orbital transformation proceudre is subject. The Boys and ER localization methods are in at least qualitative agreement for all molecules except 1,2-$C_2B_4H_6$, where the Boys localization yields a structure with fractional bonds and no open three-center B-C-B bonding. Previous ER localizations of 1,2-$C_2B_4H_6$ resulted in two open B-C-B three-center bonds and no fractional bonding.

Energy of Formation of B_2H_6 from $2BH_3$ near the Hartree-Fock Limit, D.S. Marynick, J.H. Hall Jr. and W.N. Lipscomb, J. Chem. Phys. 5460 (1974).

Using a large basis set of Gaussian orbitals, the Hartree-Fock limit for the ΔE of the reaction $2BH_3 \rightarrow B_2H_6$ is estimated to be -19.9 kcal/mole, in excellent agreement with a previously calculated value of -19.0 kcal/mole obtained with a Slater orbital basis set.

Observations Regarding Copper-Hydrogen-boron interactions in Copper Decaborane ($Cu^1)_2B_{10}H_{10}$), T.E. Paxson,* M.F. Hawthorne,* Leo D. Brown, and W.N. Lipscomb, Inorg. Chem. 13, 2772 (1974).

Both Cu-B and Cu-H-B interactions occur in the title compound. The Cu-H distances of 1.1-2.1 Å probably indicate less than full bridge bonds even though the bonding they show modifies their ir spectra in comparison with terminal B-H bonds. The ir spectra of the perdeuterated title compound and $(PPh_3)_2CuB_{10}H_{10}Cu(PPh_3)_2$ were used in conjunction with the assumed D_{4d} symmetry of the H atoms of the β polyhedra and X-ray structure determinations of related compounds in estimating the B and H positions.

*University of California at Los Angeles

Computational Evidence for a Stable Intermediate in the Rearrangement of 1,2-$C_2B_4H_6$ to 1,6-$C_2B_4H_6$, T.A. Halgren, I.M. Pepperberg, and W.N. Lipscomb, J. Am. Chem. Soc. 97, 1248 (1975).

Few reaction pathways in rearrangements of boron compounds are mechanistically well understood. The isomerization of 1,2-$C_2B_4H_6$ to 1,6-$C_2B_4H_6$ is a polyhedral rearrangement for which the cooperative twist dsd (diamond-square-diamond) mechanism has been suggested. This interconversion proceeds measurably at 250° but a CNDO/2 study failed to find an energetically accessible pathway. We report here a PRDDO study of this interconversion and of the analogous degenerate rearrangement of $B_6H_6^{2-}$ which utilizes and serves to introduce a new approach for computing reaction pathways. A principal result is a subtle but energetically significant modification of the dsd mechanism which implicates a third stable geometry on the $C_2B_4H_6$ energy surface as an intermediate in the interconversion. A second focus is the effect -- and predictability -- of carbon substitution on the energetics of the parent $B_6H_6^{2-}$ rearrangement. Based on past experience, we expect the results presented here to be of essentially ab initio minimum-basis-set quality.

Advances in Theoretical Studies of Boron Hydrides and Carboranes, W.N. Lipscomb, reprinted from Boron Hydride Chemistry (ed. E.L. Muetterties), Academic Press, San Francisco (1975), p. 39

Localized bonds and localized charges, virtual or real, in molecules and ions are now being derived from objective calculational procedures, which are rigorously based, and which also yield other molecular properties directly comparable with experiment. This recent development provides a searching test of molecular theory and is described in the area of interest here, the boranes, carboranes, and related ions. Following a brief historical introduction, sections are given on the relevant theory, on rigorous theoretical results for a number of molecular species, on the relation of these results to earlier three-center bond theory, on reactivity, and on rearrangements.

Localized Molecular Orbitals for Polyatomic Molecules. II. Structural Relationships and Charge Distributions for Open Boron Hydrides and Ions, J.H. Hall, Jr., D.A. Dixon, D.A. Kleier, T.A. Halgren, L.D. Brown and W.N. Lipscomb, J. Am. Chem. Soc. 97, 4202 (1975).

Wave functions calculated in the partial retention of diatomic differential overlap (PRDDO) approximation are presented for B_8H_{12}, B_8H_{14}, $B_8H_{13}^-$, B_9H_{15}, $B_9H_{14}^-$, $B_{10}H_{14}$, $B_{10}H_{14}^{2-}$, $B_{10}H_{13}^-$, $B_{11}H_{13}^-$, $C_2B_7H_{13}$, $C_2B_9H_{12}^-$, and $C_2B_{10}H_{13}^-$. The wave functions are analyzed in terms of the ground state charge distribution. Mulliken overlap populations, atomic and group charges, dipole moments, and ionization potentials are presented for these molecules. We compare reactivity predictions for electrophilic and nucleophilic attack at boron based on three different criteria: inner shell eigenvalues, group charges, and population sums over the highest occupied molecular orbitals. Localized molecular orbitals (LMO's) obtained using the Boys criterion are reported. The molecules are grouped into three families based on common structural features with B_8H_{12}, $B_{10}H_{14}$, and $B_{11}H_{13}^{2-}$ serving as parent molecules. Within each family, differences in LMO structure are correlated with differences in the geometrical structure and charge distribution.

Molecular Orbital Studies of Enzyme Activity: I:Charge Relay System and Tetrahedral Intermediate in Acylation of Serine Proteinases, S. Scheiner, D.A. Kleier and W.N. Lipscomb, Proc. Nat. Acad. Sci. USA 72, 2606 (1975).

The charge relay system and its role in the acylation of serine proteinases is studied using the partial retention of diatomic differential overlap (PRDDO) technique to perform approximate ab initio molecular orbital calculations on a model of the enzyme-substrate complex. The aspartate in the charge relay system is seen to act as the ultimate proton acceptor during the charging of the serine nucleophile. A projection of the potential energy surface is obtained in a subspace corresponding to this charge transfer and to the coupled motions of active site residues and the substrate. These results together with extended basis set results for cruder models suggest that a concerted transfer of protons from Ser-195 to His-57 and from His-57 to Asp-102 occurs with an energy barrier of 20-25 kcal/mole (84-105 kJ/mole). The subsequent nucleophilic attack on the scissile peptide linkage by the charged serine is then seen to proceed energetically downhill to the tetrahedral intermediate. The formation of the tetrahedral intermediate from the Michaelis complex is calculated to be nearly thermoneutral.

Localized Molecular Orbitals for Polyatomic Molecules. III. Monocyclic Aromatic Rings, D.A. Kleier, D.A. Dixon and W.N. Lipscomb, Theoret. Chim. Acta(Berl.) 40, 33 (1975).

Molecular wavefunctions have been generated by the PRDDO (Partial Retention of Diatomic Differential Overlap) method for the monocyclic aromatic rings containing six π-electrons ($C_4H_4^{-2}$, $C_5H_5^-$, C_6H_6, $C_7H_7^+$, and $C_8H_8^{+2}$) and ten π-electron species ($C_8H_8^{-2}$ $C_9H_9^-$, $C_{10}H_{10}$). The eigenvalue spectra of the canonical molecular orbitals are presented. Localized molecular orbitals (LMO's) generated using the Boys criterion are reported for localizations involving all occupied molecular orbitals (complete localizations) and localizations of the π orbitals only. We find evidence for σ-π separation in the complete localizations for some of these molecules even though the Boys criterion is often biased against such results. We demonstrate for C_6H_6 and find for the other molecules that the π-orbital localizations are indeterminate (i.e. there are an infinite number of equally satisfactory LMO structures between two limiting extremes). This result may be viewed as a corollary of Hückel's (4n+2) rule for aromaticity.

Molecular Orbital Studies of Enzyme Activity:Catalytic Mechanism of Serine Proteinases, S. Scheiner and W.N. Lipscomb, Proc. Nat. Acad. Sci.USA 73, 432 (1976).

The catalytic activity of the serine proteinases is studied using molecular orbital methods on a model of the enzyme-substrate complex. A mechanism is employed in which Ser-195, upon donating a proton to the His-57-Asp-102 dyad, attacks the substrate to form the tetrahedral intermediate. As His-57 then donates a proton to the leaving group, the intermediate decomposes to the acyl enzyme. An analogous process takes place during deacylation, as a water molecule takes the place of Ser-195 as the nucleophile. The motility of the histidine is found to be an important factor in both steps. An attempt is made to include the effects of those atoms not explicitly included in the calculations and to compare the reaction rate of the proposed mechanism with that of the uncatalyzed hydrolysis. This mechanism is found to be in good agreement with structural and kinetic data.

Localized Molecular Orbitals for Polyatomic Molecules. IV. Large Boron Hydrides, D.A. Dixon, D.A. Kleier, T.A. Halgren, and W.N. Lipscomb, J. Am. Chem. Soc. 98, 2086 (1976).

Wave functions calculated in the approximation of partial retention of diatomic differential overlap (PRDDO) are presented for $B_{13}H_{19}$, $B_{14}H_{20}$, $B_{16}H_{20}$, n-$B_{18}H_{22}$, i-$B_{18}H_{22}$, $B_{20}H_{16}$, $B_{20}H_{18}^{2-}$, and photo-$B_{20}H_{18}^{2-}$. The wavefunctions are analyzed in terms of the ground state charge distribution. Atomic and group charges, inner-shell eigenvalues on boron, dipole moments, and ionization potentials are presented for these molecules. We make and then compare reactivity predictions for electrophilic and nucleophilic attack based on group charges and inner-shell eigenvalues, neglecting steric effects, orbital control, and complex pathways. Localized molecular orbitals (LMO's) obtained using the Boys criterion are reported. These LMO structures are compared with the LMO structures obtained for the B_8 or B_{10} molecules that join together to give the larger molecule. The effects of the bonding in the fusion or bridge region are examined.

Comments on Orbital Steering, D.A. Kleier (Williams College), and S.Scheiner and W.N. Lipscomb (Harvard), Int. J. Quantum Chem.: Quantum Biology Symp No. 3 161 (1976).

Molecular orbital theory has been applied to explore the potential energy surface for several bimolecular reactions. The results of these calculations can be used to assess the rate accelerations that might be achieved in similar optimally oriented reactions. Several of the reactions studied (e.g., CH_3O^- + H_2NCHO) are bimolecular counterparts of intermediate steps in enzyme catalysis (e.g. serine proteinase activity). In these cases the importance of "orbital steering" as a vehicle for enzyme catalysis is assessed.

A Molecular Orbital Study of the Role of BH_5 in the Hydrolysis of BH_4^-, I.M. Pepperberg, T.A. Halgren, and W.N. Lipscomb, J. Am. Chem. Soc. 98, 3442 (1976).

Molecular orbital methods are employed to examine the structure and stability of BH_5 in the light of results for aqueous hydrolysis of BH_4^-. These results suggest that BH_5 exists as a metastable intermediate. The optimal BH_5 geometry for a given constraint in B-H distance is found to have C_s symmetry, and to have identifiable BH_3 and H_2 subunits consistent with the experimental expectations for the intermediate in hydrolysis. However, single determinant calculations using PRDDO and STO-3G minimum basis sets and 4-31G and double ζ plus polarization extended basis sets indicate that BH_5 is unstable with respect to dissociation to BH_3 and H_2 by $\geq$10 kcal/mol. The stabilization of BH_5 relative to BH_3 and H_2 from configuration interaction is estimated to be $\approx$10 kcal/mol. Studies of solvation effects using specific hydration and statistical interaction models indicate that the product BH_3 is stabilized in solution by $\sim$6 kcal/mol by formation of a H_2O:BH_3 complex. Representative BH_5 structures are stabilized by much smaller amounts of 2-3 kcal/mol. The net result is that the experimental and computational results cannot now be reconciled within limits of a few kilocalories per mole, presumably because of limitations in the theoretical procedures. Less sensitive aspects of the chemistry of BH_5 are examined using PRDDO, and in some cases 4-31G, calculations. These aspects include (a) a study of electronically allowed and disallowed dissociations from BH_5 of molecular hydrogen by means of various hydrogen atom pairings in each of the D_{3h}, C_{4v}, and C_{2v} structures, (b) a comparison of bonding interactions in BH_5 and CH_5^+ using localized molecular orbital techniques, and (c) a consideration of pathways for intramolecular rearrangement in C_s structures for BH_5.

Molecular Orbital Studies of Enzyme Activity. 2. Nucleophilic Attack on Carbonyl Systems with Comments on Orbital Steering, S. Scheiner, W.N. Lipscomb, (Harvard) and D.A. Kleier (Williams College), J. Am. Chem. Soc. 98, 4770 (1976).

Molecular orbital theory is applied to the study of several reactions involving nucleophilic attack at a carbonyl group. Nucleophile-carbonyl systems studied are F^- + FCHO, OH^- + FCHO, CH_3O^- + H_2NCHO, NH_3 + HCHO, CH_3OH + HCOOH, and CH_3OH + $HC(OH)_2^+$. The MO calculations are carried out at the minimum basis set level using the Partial Retention of Diatomic Differential Overlap (PRDDO) procedure. In order to assess the error associated with the minimum basis set, several calculations are repeated using an extended 4-31G basis set. The results are discussed with a critical eye toward the concept of "orbital steering."

A Theoretical Study of the Lewis-Base Adducts of Triborane(7), Leo D. Brown and W.N. Lipscomb, Inorganic Chem. 16, 1 (1977).

The Lewis-base adducts of B_3H_7 were studied using the PRDDO, STO-3G, and STO-4-31G methods. Bases used were NH_3, H_2O [as a model for $(CH_3)_2O$], $(CH_3)_2O$, and CO. Six possible structures were studied. In all cases the preferred geometry resembled the crystal structure of $B_3H_7 \cdot CO$ with one BHB bond and C_s symmetry. The weaker the base, the stronger this preference appears. The other structures did not appear to lie in local energy minima; they collapsed to the preferred geometry by a pseudorotation process. Comparison is made to the triborate ions and fluxional processes are discussed. Localized molecular orbitals, bond indices, atomic charges, and dipole moments are reported.

Extended Topological Rules for Boron Hydrides. I. Structures and Relative Energies for the Transient Boron Hydrides B_2H_4, B_3H_7, B_3H_9, B_4H_8, and B_4H_{12}, I.M. Pepperberg, T.A. Halgren and W.N. Lipscomb, Inorganic Chem. 16, 363 (1977).

Optimal geometries for the transient boron hydrides B_2H_4, B_3H_7, B_3H_9, B_4H_8, and B_4H_{12}, possible intermediates in the pyrolysis of B_2H_6, have been determined at the approximate ab initio PRDDO level and further assessed via ab initio STO-3G, Slater-orbital SCF, 4-31G, and SCF-CI calculations. Structures having one or more formally vacant orbitals are found to be preferred for the systems B_2H_4, B_3H_7, and B_4H_8 which we define as unsaturated. Preferred symmetries and topologies are D_{2d} 0012 (staggered) for B_2H_4, C_{2v} 1103 (staggered) or possibly C_s 2102 for B_3H_7, D_{3h} 3003 for B_3H_9, Cs 2112C [or possibly D_{2h} 0204 (staggered)] for B_4H_8 and D_{4h} 4004 for B_4H_{12}. An extended styx and topological formalism is developed in order to incorporate the new structures by allowing up to one vacant orbital per boron atom. The extended rules are also shown to suggest vacant orbital structures which successfully predict observed distortions from the idealized topological structures for the known hydrides, e.g., B_4H_{10}, B_5H_{11}, and $B_3H_8^-$. Bonding patterns in the transient boron hydrides are characterized via molecular orbital localizations using the criteria of Boys, and , in one case, Edmiston-Ruedenberg; and relative energies are discussed in terms of competing tendencies to maximize valency (as defined in ref. 17) and to minimize strain. An equation is presented which relates the relative energies for the transient boron hydrides to the differences in their valencies and in their topologies; the root-mean-square deviation between the predicted and observed (4-31G) relative energies is $\sim$5 kcal/mol. Nonlinear BHB bridges in the polyhedral boranes are found to be strained to the extent of $\sim$10 kcal/mol. Finally, additional justification is provided for the exclusion of open BBB bonds from the topological formalism for the boron hydrides.