on the basis of their nmr spectra contain a minor proportion of the symmetrical isomer F. This would mean that the two isomers are not resolved by gas chromatography under the conditions tried.

Noticeable differences in the infrared spectra of isomers were observed. These differences, however, cannot be interpreted on the basis of the limited evidence available at present. The spectra are consistent with the proposed structures.[10]

It has been reported recently[11] that unsymmetrically substituted borazines such as *B*-phenylpentamethylborazine undergo exchange of B substituents on distillation. No evidence of such exchange of *B*-alkyl and *B*-H substituents during distillation, gas chromatography or on standing at room temperature was obtained for the compounds described here. The purity of nmr samples was always checked by gas chromatography and was at least 96% and usually 99%. Exchange of substituents under more forcing conditions than those described here, however, was not investigated.

Experimental Section

All preparations were carried out under dry nitrogen. Solvents were dried by standard methods.

Preparation of the B-Substituted Borazines. In a typical reaction, 1,3-dimethyl-5-cyclohexylborazine[8] (6.5 g, 0.025 mol) in diethyl ether (75 ml) was treated dropwise with stirring with Grignard reagent [from magnesium (0.72 g, 0.03 mg-atom) and methyl iodide (4.2 g, 0.03 mol) in ether (75 ml)]. The reaction mixture was stirred at room temperature for 24 hr. Ether was removed under reduced pressure and the residue extracted with petroleum ether (bp 40–60°) (three 50-ml portions). The insoluble magnesium compounds were filtered off and washed with petroleum ether. The filtrate was evaporated and the residue was distilled to give a fraction, bp 66–72° (0.25 mm) (4.65 g), consisting mainly (*ca.* 80%) of compound II but also containing I, III, and IV. Yields in general were of the order of 65–75%.

Gas Chromatographic Apparatus. Analytical Apparatus. A Pye Unicam 104 Model 24 gas chromatograph with flame ionization detectors (nitrogen carrier gas) was fitted with columns (1.5 m long and 4 mm in internal diameter) packed with 10% silicone oil M.F.C. (Hopkin and Williams) on Celite, treated with hexamethyldisilazane.

Preparative Apparatus. A Pye Unicam 105 gas chromatograph was used, fitted with a column (3 m long and 1 cm in internal diameter) packed with 15% silicone oil on treated Celite. The column temperature was 190° and the nitrogen flow rate was about 180 ml/min. Solutions (50% v/v) of the distilled reaction mixtures were made up in petroleum ether (bp 40–60°). Several injections were required to obtain sufficient material for the various measurements. Only small quantities of compounds III, IV, VI, VII, and XI were obtained even after repeated injection and collection cycles, as these components were present only in low proportion (<10%) in the reaction mixtures. Chemical analyses for these compounds were thus not obtained, although they were well characterized by other methods. As the separation of compounds IX and X was especially tedious on account of their rather similar retention times, analyses for a mixture of these isomers are presented (Table I).

Combined Gas Chromatography–Mass Spectrometry. Mass spectra were recorded on a Hitachi Perkin-Elmer RMS4 mass spectrometer at 80 eV, chamber temperature 170°. Samples were introduced *via* a gas chromatograph (Perkin-Elmer F11) containing a column (1.5 m × 1-mm i.d.) packed with 10% silicone oil on Celite (80–120 mesh) at 150°. The temperature of the molecular separator (Watson-Biemann type) was 165°.

Nuclear Magnetic Resonance Spectra. Proton resonance spectra were obtained using a Varian HA-100 spectrometer at 100 MHz. Borazines were dissolved in carbon tetrachloride and chemical shifts were measured relative to internal tetramethylsilane.

Chemical Analyses. These were carried out by Dr. A. Bernhardt, Elbach uber Engelskirchen, West Germany.

Registry No. MeMgI, 917-64-6; EtMgBr, 925-90-6; I, 38126-09-9; II, 38126-11-3; III, 38126-12-4; IV, 38126-05-5; V, 38126-13-5; VI, 38126-14-6; VII, 38126-06-6; VIII, 38126-10-2; IX, 38126-15-7; X, 38126-16-8; XI, 38126-32-8; XII, 38126-17-9; XIII, 38126-04-4; XIV, 38126-33-9.

Acknowledgments. I am grateful to Dr. D. Gillies for recording the nmr spectra. A grant from the Central Research Fund, University of London, to purchase the analytical gas chromatograph used in this work is acknowledged with thanks.

---

[10] A. Meller, *Organometal. Chem. Rev.*, **2**, 1 (1967).

[11] L. A. Melcher, J. L. Adcock, and J. J. Lagowski, *Inorg. Chem.*, **11**, 1247 (1972).

Contribution from the Department of Chemistry,
Harvard University, Cambridge, Massachusetts 02138

Optimized Self-Consistent-Field and Localized Molecular Orbital Studies of Tetraborane(4)

JOHN H. HALL, Jr., IRVING R. EPSTEIN, and WILLIAM N. LIPSCOMB*

Received September 20, 1972

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/mol 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.

Introduction

The structures of the boron hydrides have been traditionally divided into two broad categories:[1] open and closed (polyhedral)[2] or, more picturesquely, basket and cage molecules.[3] The open boranes usually, but not always, have molecular formulas B_nH_{n+4} or B_nH_{n+6}, while the polyhedral boranes possess molecular formulas $B_nH_n^{2-}$. The ionic poly-

---

[1] See R. E. Williams, *Inorg. Chem.*, **10**, 210 (1971), for the names arachno, nido, and closo for B_nH_{n+6}, B_nH_{n+4}, and B_nH_{n+2}, respectively, or for their charged equivalents upon formal loss of one or more protons.

[2] W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, New York, N. Y., 1963.

[3] S. F. A. Kettle and V. Tomlinson, *J. Chem. Soc. A*, 2002, 2007 (1969).

hedral species with $n = 10, 12$ exhibit remarkable stability or even pseudo-aromaticity.[2,4] Polyhedral structures are perhaps more familiar in the extremely stable carboranes, which are derived from the parent boranes by replacing one or more B^- ions or BH groups by carbon atoms.

The chemistry and structures of the open boron hydrides have been extensively studied experimentally,[2,5] and they have been the subject of a rather thorough series of theoretical investigations.[6] The closed polyhedral molecules, particularly the carboranes, have been of great interest recently to synthetic chemists. Several remarkable compounds have been synthesized, including carborane analogs of ferrocene[7] and a fused decaborane(10)-benzene system in which the C_6 ring shows little aromaticity.[8]

Theoretical studies of polyhedral boranes have not proceeded apace, however. While a few semiempirical[9] and approximate nonempirical calculations[3,10] do exist, there is only one self-consistent field (SCF) calculation on a polyhedral borane in the literature,[11] and only several calculations on carboranes have been undertaken.[12]

Diborane(6) has been used as a model system for open boranes and a number of *ab initio* SCF calculations on these molecules using Slater exponents optimized for B_2H_6 have been carried out.[6] The availability of accurate optimized exponents from *ab initio* SCF calculations[13] and accurate bond distances obtained from electron diffraction results[14] on diborane have certainly contributed to the relatively large amount of theoretical work completed to date on the open boranes. One can attribute the relative lack of theoretical studies of polyhedral boranes, in part, to the absence of a simple prototype cage molecule which could play a role analogous to that of diborane in the series of open hydrides. Tetraborane(4) is the obvious candidate (Figure 1). The molecule has not yet been synthesized, though the substituted analog, B_4Cl_4,[15] is well known. Palke and Lipscomb[11] have previously undertaken an SCF calculation on the hypothetical B_4H_4 molecule. With the programs then available they were able to perform only a single 20-hr calculation, for which they employed Slater exponents and only one choice of estimated B-B and B-H distances.

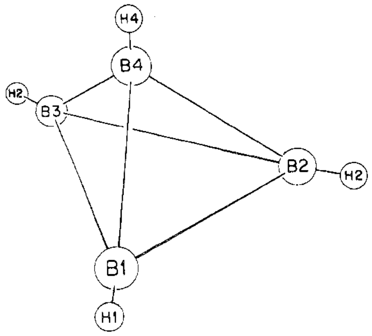

Figure 1. The geometry of B_4H_4.

With the hope of providing a model calculation for the further theoretical investigation of the polyhedral boranes, we have undertaken a recalculation of the wave function of tetraborane(4), optimizing the boron-boron distance and all atomic orbital exponents of the minimum basis set of Slater orbitals. This procedure is made possible by advances in SCF programs[16] which reduce the time for a single B_4H_4 calculation to 15 min and for a complete exponent variation calculation to 3 hr on the IBM 360/65.

Recently, methods for obtaining localized molecular orbitals (LMO's) by maximizing the self-repulsion energy[17] have received much attention. The studies have established the relationships of localized structures to those obtained from the topological theory of boron hydrides,[12b] the ability of a single configuration wave function to represent localized bonding components in molecules,[17] the construction of approximate wave functions from LMO's,[18] and the transferability of LMO's in the field of Compton scattering.[19]

We expected tetraborane(4) to provide a model system by which the transferability of LMO's to larger polyhedral boranes could be studied. However, the results of the localization described below indicate that the constraints placed upon the wave function by the high symmetry and by other aspects of the local environment have an unexpectedly great influence on the LMO's. We are only beginning to explore the effects of these constraints on simplified valence models of boranes and carboranes.

SCF Calculation

The optimized minimum basis-set wave function for B_4H_4 was determined using the SCF-LCAO method[20] and computer programs described earlier.[16] All integrals were evaluated to an accuracy of five decimal places. Although the symmetry of the molecule is assumed by us to be T_d, the calculation was made in the C_{3v} subgroup as a matter of convenience. Slater orbitals, but not Slater exponents, formed the atomic basis. In the previous LCAO calculation on B_4H_4 by Palke and Lipscomb[11] the B-B distance in B_4Cl_4 of 1.74 Å and a B-H distance of 1.20 Å were chosen. Here, we

---

(4) (a) R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, 36, 2179 (1962); (b) E. L. Muetterties and W. H. Knoth, "Polyhedral Boranes," Marcel Dekker, New York, N. Y., 1968, pp 78-79.

(5) See G. R. Eaton and W. N. Lipscomb, "NMR Studies of Boron Hydrides and Related Compounds," W. A. Benjamin, New York, N. Y., 1969, for a review.

(6) (a) I. R. Epstein, J. A. Tossell, E. Switkes, R. M. Stevens, and W. N. Lipscomb, *Inorg. Chem.*, 10, 171 (1971), and references therein; (b) W. N. Lipscomb, *Pure Appl. Chem.*, 29, 493 (1972).

(7) (a) M. F. Hawthorne, D. C. Young, and P. A. Wegner, *J. Amer. Chem. Soc.*, 87, 1818 (1965); (b) M. F. Hawthorne and T. D. A. Andrews, *Chem. Commun.*, 443 (1965); (c) the σ- and π-bonding potential of B_{11} (or B_9C_2) frameworks was developed by E. B. Moore, Jr., L. L. Lohr, Jr., and W. N. Lipscomb, *J. Chem. Phys.*, 35, 1329 (1961).

(8) D. S. Matteson and N. K. Hota, *J. Amer. Chem. Soc.*, 93, 2893 (1971).

(9) C. C. S. Cheung, R. A. Beaudet, and G. A. Segal, *J. Amer. Chem. Soc.*, 92, 4158 (1970).

(10) T. F. Koetzle and W. N. Lipscomb, *Inorg. Chem.*, 9, 2743 (1970).

(11) W. E. Palke and W. N. Lipscomb, *J. Chem. Phys.*, 45, 3945 (1966).

(12) (a) I. R. Epstein, T. F. Koetzle, R. M. Stevens, and W. N. Lipscomb, *J. Amer. Chem. Soc.*, 92, 7019 (1970); (b) D. S. Marynick, I. R. Epstein, and W. N. Lipscomb, unpublished results; (c) D. S. Marynick and W. N. Lipscomb, *J. Amer. Chem. Soc.*, 94, 1748 (1972).

(13) E. Switkes, R. M. Stevens, and W. N. Lipscomb, *J. Chem. Phys.*, 51, 2085 (1969).

(14) L. S. Bartell and B. L. Carroll, *J. Chem. Phys.*, 42, 1135 (1964).

(15) (a) G. Urry, T. Wartik, and H. I. Schlesinger, *J. Amer. Chem. Soc.*, 74, 5809 (1952); (b) M. Atoji and W. N. Lipscomb, *J. Chem. Phys.*, 21, 172 (1953); *Acta Crystallogr.*, 6, 547 (1953).

(16) R. M. Stevens, *J. Chem. Phys.*, 52, 1937 (1970).

(17) (a) C. Edmiston and K. Ruedenberg, *J. Chem. Phys.*, 43, S97 (1965); C. Edmiston and K. Ruedenberg in "Quantum Theory of Atoms, Molecules and the Solid State," P. -O. Lowdin, Ed., Academic Press, New York, N. Y., 1966; (b) R. M. Pitzer, *J. Chem. Phys.*, 41, 2216 (1964); (c) U. Kaldor, *ibid.*, 46, 1981 (1967); (d) C. Trindle and O. Sinanoglu, *ibid.*, 49, 65 (1968); *J. Amer. Chem. Soc.*, 91, 853 (1969); (e) S. Rothenberg, *J. Chem. Phys.*, 51, 3389 (1969); (f) W. England and M. Gordon, *J. Amer. Chem. Soc.*, 91, 6864 (1969).

(18) (a) E. Switkes, R. M. Stevens, W. N. Lipscomb, and M. D. Newton, *J. Chem. Phys.*, 51, 2085 (1969); (b) E. Switkes, W. N. Lipscomb, and M. D. Newton, *J. Amer. Chem. Soc.*, 92, 3847 (1970); (c) M. D. Newton, E. Switkes, and W. N. Lipscomb, *J. Chem. Phys.*, 53, 2645 (1970); (d) M. D. Newton and E. Switkes, *ibid.*, 54, 3179 (1971).

(19) I. R. Epstein, *J. Chem. Phys.*, 53, 4425 (1970).

(20) C. C. J. Roothaan, *Rev. Mod. Phys.*, 23, 69 (1951).

Table I. Coordinates of Unique Atoms (au)[a]

	x	y	z
B1	1.85488	0.0	−0.65563
B4	0.0	0.0	1.96734
H1	3.97512	0.0	−1.40506
H4	0.0	0.0	4.21613

[a] The molecule of T_d symmetry is oriented with the B_4–H_4 bond along z. These coordinates reflect the C_{3v} subgroup assumed for convenience in the SCF calculation.

Table II. Optimized Exponents and Energy Analysis[a]

		Energy analysis	
	Exponents	Energy	Value
B 1s	4.686	Electronic energy	−168.7280
B 2s	1.386	Nuclear repulsion	67.9682
B 2p	1.389	Total energy	−100.7598
H_t 1s	1.173	Kinetic energy	100.7235
		$-E/T$	1.0004
		IP	0.398
		Atomization energies	−0.776[b]
			−0.930[c]

[a] All quantities are in atomic units. [b] The reference atoms use Clementi's best single-ζ exponents: $E(\mathrm{B}) = -24.4984$, $E(\mathrm{H}) = -0.500$. [c] The reference atoms employ B_4H_4 molecular exponents: $E(\mathrm{B}) = -24.4724$, $E(\mathrm{H}) = -0.4850$.

assumed a B–H distance of 1.19 Å[6] and optimized the B–B distance to the value of 1.70 Å. Coordinates of the unique boron and hydrogen atoms are given in Table I.

The final values of the exponents are given in Table II. The H 1s, B 2p, B 2s, and B 1s exponents were respectively chain optimized until convergences of 0.0001 au in the energy and 0.02 au in the exponents were achieved. Results obtained using exponents from this optimized calculation show that B_4H_4 is stable relative to four BH units by 316.89 kcal/mol in this rather crude approximation. Furthermore, the SCF energy of B_4H_4 is lowered by 37.5 kcal/mol when the optimized exponents are used instead of the exponents from diborane. It seems likely that a definite improvement in the energy, and thus in the wave function, can be obtained from calculations on polyhedral molecules if B_4H_4 rather then B_2H_6 is used as a source of parameters.

Energetics

The total energies, virial ratio, ionization potential, and atomization energies are listed in Table II. Atomization energies are calculated from Clementi's[21] best single-ζ atomic energies and from atomic energies obtained from SCF wave functions for boron and hydrogen using the optimized B_4H_4 exponents. The atomization energies calculated from the second method agree quite well with experiment for known boron hydrides,[6] although the agreement is due to a fortuitous cancelation of errors. Orbital energies and orbital coefficients are given in Table III.

Population Analysis and Density Maps

The Mulliken[22] atomic charges and the overlap and orbital populations are presented in Table IV. The atomic charges in our optimized calculation are reversed in sign and smaller in magnitude than those calculated by Palke and Lipscomb. Nevertheless, the negative charge on the hydrogen is consistent with the finding that in SCF studies of this quality, all terminal hydrogens are slightly negatively charged. However, the charge on boron is quite small in magnitude as compared with results of the previous calculations on other hydrides. Overlap populations of 0.492 for B–B and 0.824 for B–H also reflect the change to the optimized basis set. Total electron density contours are given for the B_1-B_2-B_3 plane and the H_1-B_1-B_2 plane, respectively, in Figures 2 and 3. The symmetry of the *total* density in the B_1-B_2-B_3 plane is immediately apparent.

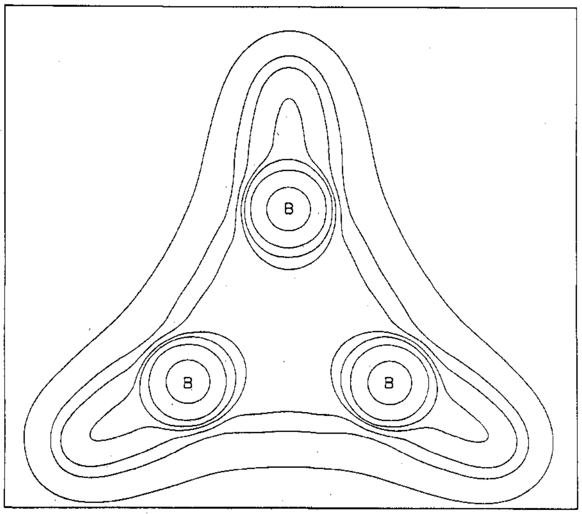

Figure 2. Total electron density in a B–B–B plane of B_4H_4. Contours are at 3.0, 0.30, 0.17, 0.14, 0.11, 0.09, and 0.05 e/au^3.

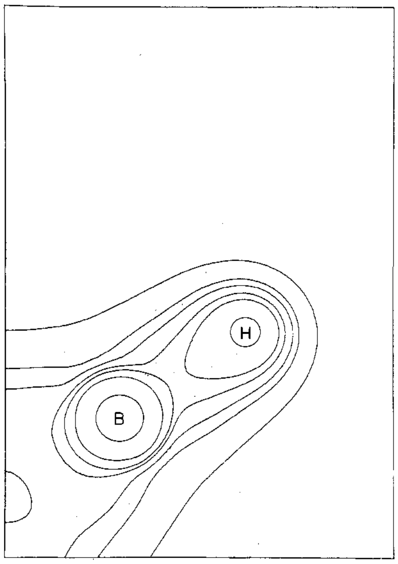

Figure 3. Total electron density for a B–H bond of B_4H_4. Contours are at 3.0, 0.30, 0.17, 0.14, 0.11, 0.09, and 0.05 e/au^3, assuming two-electron occupancy.

The SCF calculation does not offer any obvious indication that B_4H_4 is unstable, except, possibly, for the vacant E pair of orbitals at $\epsilon = 0.0552$ au. The molecule is bound relative to four BH units, and it shows a minimum in the energy surface when the B–B bond distance is optimized. Of course, we have not studied other distortions, nor have we explored probable transition states in encounters with the same or different molecules. Both experimental and further theoretical studies are desirable.

Localized Orbitals

The localization calculation was performed using the Edmiston-Ruedenberg (ER) procedure[17a] for obtaining localized molecular orbitals (LMO's). Successive 2 × 2 unitary transformations were applied to the canonical mole-

---

(21) E. Clementi and D. L. Raimondi, *J. Chem. Phys.*, 38, 686 (1963).

(22) R. S. Mulliken, *J. Chem. Phys.*, 36, 3428 (1962).

Table III. B_4H_4 Occupied and Unoccupied Molecular Orbitals and Energies

	1	2	3	4	5	6	7	8	9	10	11	12
	A1	T1	T1	T1	A1	T1	T1	T1	A1	T1	T1	T1
	-7.6277	-7.6269	-7.6269	-7.6269	-0.9372	-0.6097	-0.6097	-0.6097	-0.5772	-0.3981	-0.3981	-0.3981
B1-1S	0.4999	0.8122	0.0000	-0.2830	0.1240	0.1435	0.0000	-0.0507	-0.0269	0.0490	0.0000	-0.0173
B1-2S	0.0070	0.0259	0.0000	-0.0091	-0.2365	-0.4368	0.0000	0.1545	0.1352	-0.2328	0.0000	0.0823
B1-2PZ	0.0001	0.0008	0.0000	-0.0038	-0.0552	0.0283	0.0000	-0.1266	-0.0856	-0.2376	0.0000	-0.2926
B1-2PX	-0.0001	-0.0058	0.0000	0.0008	0.1562	-0.1968	0.0000	0.0284	0.2421	0.2954	0.0000	-0.2376
B1-2PY	0.0000	0.0000	-0.0035	0.0000	0.0000	0.0000	-0.1166	0.0000	0.0000	0.0000	-0.3766	0.0000
B2-1S	0.4999	-0.4061	0.7034	-0.2830	0.1240	-0.0718	0.1243	-0.0507	-0.0269	-0.0245	0.0424	-0.0173
B2-2S	0.0070	-0.0130	0.0224	-0.0091	-0.2365	0.2184	-0.3783	0.1545	0.1352	0.1164	-0.2016	0.0823
B2-2PZ	0.0001	-0.0004	0.0007	-0.0038	-0.0552	-0.0142	0.0245	-0.1266	-0.0856	0.1188	-0.2057	-0.2926
B2-2PX	0.0000	-0.0041	0.0010	-0.0004	-0.0781	-0.1366	0.0347	-0.0142	-0.1211	-0.2086	-0.2910	0.1188
B2-2PY	-0.0001	0.0010	-0.0052	0.0007	0.1352	0.0347	-0.1767	0.0246	0.2097	-0.2910	0.1274	-0.2057
B3-1S	0.4999	-0.4061	-0.7034	-0.2830	0.1240	-0.0718	-0.1243	-0.0507	-0.0269	-0.0245	-0.0424	-0.0173
B3-2S	0.0070	-0.0130	-0.0224	-0.0091	-0.2365	0.2184	0.3783	0.1545	0.1352	0.1164	0.2016	0.0823
B3-2PZ	0.0001	-0.0004	-0.0007	-0.0038	-0.0552	-0.0142	-0.0245	-0.1266	-0.0856	0.1188	0.2057	-0.2926
B3-2PX	0.0000	-0.0041	-0.0010	-0.0004	-0.0781	-0.1366	-0.0347	-0.0142	-0.1211	-0.2086	0.2910	0.1188
B3-2PY	0.0001	-0.0010	-0.0052	-0.0007	-0.1352	-0.0347	-0.1767	-0.0246	-0.2097	0.2910	0.1274	0.2057
B4-1S	0.4904	0.0000	0.0000	0.8656	0.1240	0.0000	0.0000	0.1522	-0.0269	0.0000	0.0000	0.0520
B4-2S	0.0067	0.0000	0.0000	0.0275	-0.2365	0.0000	0.0000	-0.4633	0.1352	0.0000	0.0000	-0.2469
B4-2PZ	-0.0000	0.0000	0.0000	-0.0061	0.1657	0.0000	0.0000	-0.2068	0.2568	0.0000	0.0000	0.3794
B4-2PX	0.0000	-0.0035	0.0000	0.0000	0.0000	-0.1166	0.0000	0.0000	0.0000	-0.3766	0.0000	0.0000
B4-2PY	0.0000	0.0000	-0.0035	0.0000	0.0000	0.0000	-0.1166	0.0000	0.0000	0.0000	-0.3766	0.0000
H1-1S	-0.0014	-0.0030	0.0000	0.0010	-0.0553	-0.3806	0.0000	0.1346	0.2469	0.2632	0.0000	-0.0930
H2-1S	-0.0014	0.0015	-0.0026	0.0010	-0.0553	0.1903	-0.3296	0.1346	0.2469	-0.1316	0.2279	-0.0930
H3-1S	-0.0014	0.0015	0.0026	0.0010	-0.0553	0.1903	0.3296	0.1346	0.2469	-0.1316	-0.2279	-0.0930
H4-1S	-0.0014	0.0000	0.0000	-0.0032	-0.0553	0.0000	0.0000	-0.4037	0.2469	0.0000	0.0000	0.2792

	13	14	15	16	17	18	19	20	21	22	23	24
	E	E	T2	T2	T2	T1	T1	T1	A1	T1	T1	T1
	0.0552	0.0552	0.4343	0.4343	0.4343	0.5157	0.5157	0.5157	0.5271	0.8447	0.8447	0.8447
B1-1S	0.0000	0.0000	0.0000	0.0001	0.0000	0.1986	0.0000	-0.0702	0.0489	0.0361	0.0000	0.0128
B1-2S	-0.0000	0.0000	0.0000	-0.0006	0.0000	-1.5004	0.0000	0.5308	-0.4870	-0.4006	0.0000	-0.1417
B1-2PZ	0.4590	0.0000	0.0000	0.8173	0.0000	0.0726	0.0000	0.3953	0.1446	-0.3765	0.0000	-0.4234
B1-2PX	0.1623	0.0000	0.0000	0.2890	0.0000	0.2146	0.0000	0.0732	-0.4083	1.3552	0.0000	0.3765
B1-2PY	0.0000	-0.4869	0.8173	0.0000	0.2892	0.0000	0.4211	0.0000	0.0000	0.0000	0.2902	0.0000
B2-1S	0.0000	0.0000	0.0000	-0.0000	0.0001	-0.0993	0.1720	-0.0702	0.0489	-0.0180	0.0313	0.0128
B2-2S	0.0000	-0.0000	0.0000	0.0003	-0.0005	0.7502	-1.2993	0.5308	-0.4870	0.2003	-0.3469	-0.1417
B2-2PZ	-0.2295	0.3975	0.0000	-0.4087	0.7078	-0.0363	0.0629	0.3953	0.1446	0.1882	-0.3260	-0.4234
B2-2PX	-0.3246	-0.2811	-0.7078	0.2891	0.0001	0.3695	0.0894	-0.0366	0.2042	0.5565	-0.4611	-0.1883
B2-2PY	-0.2811	-0.0000	-0.4086	0.0001	0.2891	0.0894	0.2662	0.0634	-0.3536	-0.4611	1.0889	0.3261
B3-1S	0.0000	0.0000	0.0000	-0.0000	-0.0001	-0.0993	-0.1720	-0.0702	0.0489	-0.0180	-0.0313	0.0128
B3-2S	0.0000	0.0000	0.0000	0.0003	0.0005	0.7502	1.2993	0.5308	-0.4870	0.2003	0.3469	-0.1417
B3-2PZ	-0.2295	-0.3975	0.0000	-0.4087	-0.7078	-0.0363	-0.0629	0.3953	0.1446	0.1882	0.3260	-0.4234
B3-2PX	-0.3246	0.2811	0.7078	0.2891	-0.0001	0.3695	-0.0894	-0.0366	0.2042	0.5565	0.4611	-0.1883
B3-2PY	0.2811	-0.0000	-0.4086	-0.0001	0.2891	-0.0894	0.2662	-0.0634	0.3536	0.4611	1.0889	-0.3261
B4-1S	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.2106	0.0491	0.0000	0.0000	-0.0383
B4-2S	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	-1.5912	-0.4881	0.0000	0.0000	0.4252
B4-2PZ	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.1891	-0.4330	0.0000	0.0000	-1.4883
B4-2PX	0.4868	0.0000	0.0000	-0.8667	0.0000	0.4216	0.0000	0.0000	0.0000	0.2903	0.0000	0.0000
B4-2PY	0.0000	0.4868	0.0000	0.0000	-0.8667	0.0000	0.4216	0.0000	0.0000	0.0000	0.2903	0.0000
H1-1S	0.0000	0.0000	0.0000	0.0003	0.0000	0.7006	0.0000	-0.2481	0.6720	-0.8857	0.0000	-0.3131
H2-1S	0.0000	0.0000	0.0000	-0.0001	0.0003	-0.3503	0.6067	-0.2481	0.6720	0.4429	-0.7671	-0.3131
H3-1S	0.0000	0.0000	0.0000	-0.0001	-0.0003	-0.3503	-0.6067	-0.2481	0.6720	0.4429	0.7671	-0.3131
H4-1S	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.7428	0.6725	0.0000	0.0000	0.9394

Table IV. Atomic Charges and Overlap and Orbital Populations

	Atomic charges		Overlap populations	
	I[a]	II[b]	I[a]	II[b]
B	+0.0046	-0.08	0.492	0.451 (B-B)
H	-0.0046	+0.08	0.824	0.837 (B-H)

	Orbital populations				
	1s	2s	$2p_x$	$2p_y$	$2p_z$
B1	1.994	0.998	0.868	0.551	0.591
B2	1.994	0.998	0.631	0.789	0.591
B3	1.994	0.998	0.631	0.789	0.591
B4	1.994	0.998	0.551	0.551	0.908
H	1.004				

[a] This calculation. [b] Reference 11.

cular orbitals (CMO's), which result from the SCF calculation, in order to maximize the self-repulsion energy

$$J = \sum_i \langle ii|ii\rangle = \sum_i \int \phi_i(1)\phi_i(1)\frac{1}{r_{12}}\phi_i(2)\phi_i(2)\,dv_1dv_2 \tag{1}$$

This procedure is thus completely *ab initio*. The uniqueness of the calculations was then tested by repeating the calculation several times, after subjecting the initial CMO's to different initial random unitary transformations.[18a] Iterations were continued until we obtained a convergence of the LMO coefficients, which provide a much more stringent convergence test than does the self-repulsion energy.

The self-repulsion energy can be expanded about an extremum in powers of a scalar parameter ϵ[23]

$$J = J_0 + \epsilon J_1 + \epsilon^2 J_2 + \ldots \tag{2}$$

where

$$J_0 = \sum_i \langle ii|ii\rangle$$

$$J_1 = \sum_{i>j} 4[\langle ii|ij\rangle - \langle jj|ji\rangle]A_{ji} \tag{3}$$

The A_{ji} are the $n(n-1)/2$ independent elements which define a unitary matrix. For any localization procedure which maximizes J, the requirement that the calculation be at an extremum is

$$\nabla J = \left\{\sum_{i>j}[\langle ii|ij\rangle - \langle jj|ji\rangle]^2\right\}^{1/2} = 0 \tag{4}$$

This condition requires that the first-order term vanishes. However, one must realize that localized orbitals are not the only type of orbitals which satisfy (4). For example, the benzene localization[18d] appears to have converged to a saddle point when σ-π separation was imposed, yielding

---

(23) W. J. Taylor, *J. Chem. Phys.*, 48, 2385 (1968).

LMO's which are actually symmetry-equivalent orbitals. Symmetry-equivalent orbitals will satisfy (4), giving zero for all $n(n-1)/2$ first derivatives of the self-energy surface;[18b] but the calculation may be at a saddle point and not a true maximum.

Although B_4H_4 is a hypothetical molecule and has a simple but highly symmetrical proposed tetrahedral structure, the LMO's obtained from the ER procedure are quite interesting for at least three reasons. First, localization of B_4H_4 yields four three-center BBB bonds which are asymmetrical (Table V). These four different BBB bonds on the tetrahedral faces are, however, nearly equivalent in terms of delocalization percentages (Table V), defined as [18b]

$$d = [{}^1\!/_2 \int (\phi^{\mathrm{T}} - \phi)^2 \, \mathrm{d}v]^{1/2} \times 100\%$$

where ϕ is an LMO and ϕ^{T} is obtained from ϕ by truncating the nonlocal contributions to ϕ and renormalizing. Second, the B-H bonds are not only unequivalent in terms of orbital populations, but they are also 1.5-2 times more delocalized than B-H bonds in any previous localization (Table V). Third, 33 iterations were required before the convergence criterion was met. For comparison, the diborane localization required only 5 iterations, and the final gradient of the self-energy surface in the direction of steepest ascents for B_2H_6 was several orders of magnitude smaller than that of B_4H_4. Values of the gradient and self-repulsion energy after 5, 15, 30, and 33 iterations are given in Table VI to illustrate this slow rate of convergence for B_4H_4. The final energy analysis for B_4H_4 is given in Table VII.

Discussion

In a localization procedure there is always a possibility of convergence to a minimum which may not be the lowest of all possible minima. The several starting points, most of which were generated from a random unitary transformation of the CMO's, make this possibility unlikely but do not eliminate it. Nevertheless, we shall discuss the surprising features of the localization in B_4H_4 believing that we have indeed found the lowest minimum in the self-repulsion energy.

Perspective on the percentages of delocalization is gained by comparison with earlier studies. External B-H bonds in boron hydrides show d values of 9-10%. Even the B-H bonds extending toward the open face of B_5H_{11} show d values of only 14% (to nonapex B) and 20% (to apex B). Hence, the values for B-H bonds in B_4H_4 are unusual indeed (Table V). The values of d for the BBB bonds are somewhat high but not unusual. Delocalization percentages for three-center bonds in B_5H_9 (d = 20-22%), in B_5H_{11} (d = 20%), and in B_6H_{10} (d = 20%) are only somewhat smaller than those shown in Table V.

An analysis of the $n(n-1)/2$ terms in eq 4 shows that, after convergence, the major contribution to the self-repulsion energy arises from the B-H bonds in B_4H_4. Therefore, these B-H bonds are more weakly coupled to the self-repulsion energy than are the BBB bonds. Ambiguous localizations, primarily in framework bonding, have appeared earlier[12b,18b] in other molecules having high symmetry. These molecules (B_5H_9 and 1,6-$C_2B_4H_6$) were similar to B_4H_4 in the sense that some LMO's were weakly coupled to the self-repulsion energy, and they gave d values nearly as high as that shown for the BBB bonds in B_4H_4. Perhaps the one common feature is the constraint that the geometrical symmetry exerts. In a molecule of low symmetry the LMO's appear to delocalize in order to approach the molecular symmetry, within the other constraints discussed below, while in a molecule of high geometrical symmetry these other constraints prevent the LMO's from localizing to the full molecular symmetry. Extreme cases are three framework pairs in B_5H_9 and seven framework pairs in 1,6-$C_2B_4H_6$, both in situations where a fourfold axis exists in the molecule. The essence of localization is the mixing of orbitals of different symmetry classes in order to keep electron pairs away from pairs in other orbitals.

Table V. Per Cent Delocalization and Orbital Populations for Localized Orbitals[a]

Bond	d	Orbital populations		
B_1-H_1	22.3	0.912	0.918	
B_2-H_2	29.5	0.844	0.849	
B_3-H_3	40.8	0.728	0.663	
B_4-H_4	35.8	0.776	0.751	
B_1-B_2-B_3	20.9	0.759	0.727	0.409
B_2-B_3-B_4	18.7	0.735	0.721	0.542
B_1-B_3-B_4	21.4	0.653	0.758	0.536
B_1-B_2-B_4	21.2	0.570	0.514	0.815

[a] The values for d in ref 6 and 18b were found to be in error by a factor of $2^{1/2}$; thus, the d values in ref 6 and 18b should be multiplied $2^{1/2}$ when comparing them with the d values in this table.

Table VI. Gradient of the Self-Energy and the Self-Energy after 5, 15, 30, and 33 Iterations (au)

Iterations	J	∇J[a]
5	14.969704	0.00706
15	14.969960	0.00656
30	14.971826	0.000479
33	14.971883	0.000280

[a] Calculated using eq 4.

Table VII. Localization Energy Analysis (au)

	CMO's	LMO's
Total two-electron energy	98.6352	98.6352
Coulomb energy	106.6238	100.5925
Exchange energy	−7.9886	−1.9573
Self-energy	8.9405	14.9719

The two additional constraints on the wave function are that the total electron density remain constant and that the LMO's remain orthogonal after a transformation. Constancy of density is a matter of charge conservation and therefore cannot be violated. However, orthogonality of the LMO's is largely a computational convenience, and relaxation of this constraint may merit further study.

The high symmetry of B_4H_4, these additional constraints, and the weak coupling of the external B-H bonds then direct attention to the framework bonds. We find here that four symmetrical three-center BBB bonds, one in each face of the tetrahedron, give a lower self-repulsion energy than do the localized bonds (Table V). Some tendency toward direct bonding along edges B_1-B_2, B_2-B_3, and B_1-B_3, with a slightly high concentration of charge on B_4, seems to occur. Rather than form symmetrical three-center bonds, the tetrahedral B_4H_4 molecule appears to try to concentrate the localized bonding pairs along edges, insofar as it can within the strong constraints noted above. The result is quite unsymmetrical three-center framework BBB bonds and large perturbations in the external BH bonds which are weakly coupled to the self-repulsion energy. In summary, the asymmetries in these BBB bonds can be attributed to a failure to minimize interbond repulsions sufficiently when the unique topological structure[24] (the symmetrical three-center bond) is forced on each face of the regular tetrahedron.

We are as yet unprepared to say whether this unexpected

---

(24) I. R. Epstein and W. N. Lipscomb, *Inorg. Chem.*, 10, 1921 (1971).

pathology of localized bonding in B_4H_4 is related to its nondiscovery. Studies of localized orbitals in reactions, intermediates, and transition states may be useful, especially in reactions in which pairing schemes are conserved. Perhaps the only clear experimental fact is that B_4Cl_4 does exist, and we suggest that a study, which may soon be possible, of localized orbitals in this molecule may be of interest. There is a set of vacant E orbitals in B_4H_4 at an eigenvalue of only 0.055 au, perhaps placing this molecule in the vacant-orbital class, like BH_3. Back-π-bonding is possible in BCl_3, but not in BH_3, which dimerizes to B_2H_6. Longuet-Higgins[25] has shown that the E pair is of the appropriate symmetry to accept localized back-π-donation from Cl in B_4Cl_4, and he suggested that B_4Cl_4 might be stabilized in a way that B_4H_4 cannot. This is a more detailed and informative statement than the topological theory of King,[26] who proposed that vertices of order 3 (boron bound to three other borons) should result in molecular instability. The existence of B_4Cl_4 is inconsistent with this proposal of King and is also not compatible with his contention that stable, closed neutral borane frameworks must have either BH_2 groups or bridge hydrogens. Thus, purely topological arguments shed little light on the B_4H_4 problem.

In conclusion, B_4H_4 should be one of a reasonable set of molecules to serve as a prototype for future SCF calculations on polyhedral boranes and carboranes. Analysis of the B_4H_4 localization indicates that the LMO's are, in some cases, very dependent on symmetry and other constraints placed upon LMO's. Thus one should be extremely careful with regard to similarity of local chemical environment and molecular symmetry when constructing approximate molecular wave functions from the localized bond components.[27]

Registry No. B_4H_4, 27174-99-8.

Acknowledgments. We wish to thank the Office of Naval Research for support of this work and D. S. Marynick for many helpful discussions and for the use of several of his computer programs. I. R. E. thanks the National Science Foundation for a predoctoral fellowship.

---

(25) H. C. Longuet-Higgins, *Quart. Rev., Chem. Soc.*, 11, 121 (1957).

(26) R. B. King, *J. Amer. Chem. Soc.*, 94, 95 (1972).

(27) Note Added in Proof. *Ab initio* SCF calculations have been completed on the molecules B_4F_4 and B_4Cl_4. We will publish the results shortly.

Contribution from the Evans Chemical Laboratories,
The Ohio State University, Columbus, Ohio 43210

Preparation and Proposed Structure for Bis[bis(dimethylamino)bromoborane]-Tris(titanium tetrabromide)

M. R. SULIMAN[1] and E. P. SCHRAM*

Received September 20, 1972

Treatment of $[(CH_3)_2N]_2BBr$ with $TiBr_4$ affords $\{[(CH_3)_2N]_2BBr\}_2\{TiBr_4\}_3$. The stoichiometry of the latter was established by determination of the reactant ratio and by nucleophilic degradation affording $TiBr_4 \cdot N(CH_3)_3$ and $[(CH_3)_2N]_2BBr$. A structure is proposed for $\{[(CH_3)_2N]_2BBr\}_2\{TiBr_4\}_3$ based on infrared assignments and the unusual stoichiometry of this compound.

Introduction

Treatment of $TiCl_4$ with $[(CH_3)_2N]_2BCl$ has been reported to afford the labile species $\{[(CH_3)_2N]_2BCl\}_2\{TiCl_4\}_3$ (I).[2] Several possible structures were suggested including an ionic formulation involving hexachlorotitanate, $TiCl_6^{2-}$, as well as two different molecular formulations with $[(CH_3)_2N]_2BCl$ moieties bridging between three $TiCl_4$ species. One example of the latter consisted of all three Ti being six-coordinate with single Cl bridges, whereas the other involved mixed five- and six-coordinate Ti with no Cl bridges. Based on the ease of dissociation of I, a molecular formulation was favored rather than one involving ionic species. The reaction of $TiBr_4$ with $[(CH_3)_2N]_2BBr$ was investigated in order to prepare a compound stoichiometrically analogous to I but with the larger Br moieties more sterically limiting compared to those of Cl, thus allowing a distinction between molecular structures.

Experimental Section

Equipment. Chemical reactions and procedures were followed as previously described while infrared spectra were recorded with a Perkin-Elmer 457 spectrometer employing KBr and CsBr cell windows.[2]

Reagents. Bis(dimethylamino)bromoborane, $[(CH_3)_2N]_2BBr$, was prepared by treatment of BBr_3 with a twofold molar excess of tris(dimethylamino)borane, $[(CH_3)_2N]_3B$, in *n*-pentane.[3] The reaction mixture was stirred for 3 hr followed by removal of solvent under vacuum, affording a colorless liquid which was distilled in the range 35–37° (2 Torr), lit.[3] 25–28° (0.5 Torr). Infrared data: 3015 (ms), 2940 (s, sh), 2900 (vs), 2820 (ms), 1555 (s, sh), 1535 (vvs), 1482 (w, sh), 1465 (vs), 1412 (vvs), 1408 (vs, sh), 1358 (vs), 1212 (vvs), 1195 (s, sh), 1185 (w, sh), 1145 (vvs), 1118 (w, sh), 1070 (vvs), 900 (s, sh), 880 (ms), 838 (s), 582 (w, sh), and 565 (ms) cm^{-1}.

Tris(dimethylamino)borane, $[(CH_3)_2N]_3B$, was prepared by the treatment of BCl_3 with more than a sixfold molar excess of $HN(CH_3)_2$.[4] The resulting liquid was freed of any traces of bis(dimethylamino)chloroborane, $[(CH_3)_2N]_2BCl$, by further treatment with $HN(CH_3)_2$ followed by fractional distillation through a −22° trap into one at −196°. Tris(dimethylamino)borane recovered from the −22° trap was identified by its vapor-phase infrared spectrum[5] and by its 25° vapor tension of 5.2 Torr, lit.[6] 5.2 Torr.

---

(1) In partial fulfillment of the Ph.D. degree, The Ohio State University, 1971.

(2) G. S. Kyker and E. P. Schram, *J. Amer. Chem. Soc.*, 90, 3672 (1968).

(3) R. J. Brotherton, *J. Amer. Chem. Soc.*, 82, 6242 (1960).

(4) J. Goubeau, M. Rahtz, and H. J. Becher, *Z. Anorg. Allg. Chem.*, 275, 161 (1954).

(5) G. S. Kyker and E. P. Schram, *J. Amer. Chem. Soc.*, 90, 3678 (1968).

(6) E. Wiberg and K. Schuster, *Z. Anorg. Allg. Chem.*, 213, 77 (1933).