differ between the two conformations. The calculated dipole had a value of 2.53 D which is considerably larger than the experimental value of 1.74 D. This discrepancy is somewhat larger than one would expect from such calculations. The calculations indicated that the dipole resulted mainly from the electron densities rather than from the polarizations. The distribution of the electronic charge was found for the planar form to be: $H_{1\beta}$, 1.00; $H_{2\beta}$, 1.01; H_{α}, 0.97; C_{α}, 4.16; C_{β}, 3.87; B, 2.44; F_1, F_2, 7.28. These data may indicate that the nonbonded interactions between the fluorine and hydrogen atoms play a significant role in the stabilization of the planar configuration. The calculated energy difference between the two forms was found to be 1.2 kcal/mol which agrees with the experimental value about as well as would be expected for these type of calculations.

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Registry No. $CH_2CH^{11}BF_2$, 43199-85-5; $CH_2CH^{10}BF_2$, 43199-86-6; CH_2CHBF_2, 358-95-2.

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Hexamethylenetetramine-Borane Adducts

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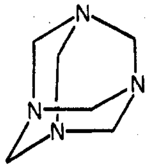
The four possible borane adducts of hexamethylenetetramine (hexamine) were prepared, three of which being hitherto unknown. Synthesis and purification procedures were worked out so that pure samples were available for chemical studies. Pyrolysis of the tetraadduct when controlled proceeded with rearrangement by hydride migration to form dimethylaminoborane derivatives. The adducts were not amenable to borane cation formation; those two cations eventually prepared, $(CH_2)_6N_4BH_2py^+$ and $(CH_2)_6N_4BH_2P(CH_3)_3^+$, were not very stable.

The four equivalent tertiary nitrogen sites in hexamine (hexamethylenetetramine) offer interesting possibilities for multiple borane adducts. Moreover, adduct formation on vicinal base sites in this molecule might lead to charge build up and subsequent rearrangement.



A monoadduct, $(CH_2)_6N_4 \cdot BH_3$, has previously been isolated in small yield (15%) from aqueous solutions of sodium borohydride and hexamine[2] or hexamine hydrochloride.[3] No other hexamine adducts have been reported, but bisborane adducts are known for ethylenediamine[4] and its *N*-methyl derivatives[5] as well as the analogous propanediamine bases[6] and *N,N'*-dimethylpiperazine (DMP).[7] These fully boranated adducts are air-stable, sublimable white solids in general. Some can be recrystallized from suitable solvents like acetonitrile.

Higher borane adducts of polyamines have been examined in neutron capture applications.[8] (^1H is the most effective element for moderating neutrons while ^{10}B has the highest capture cross section of the light elements.) The adducts prepared were: pentamethyldiethylenetriamine-trisborane, mp 185-186°; hexamethyltriethylenetetramine-bisborane, mp 118.5-119.5°; hexamethyltriethylenetetramine-tetrakisborane, mp 208-220°; pentamethyldi-*n*-propylenediamine-trisborane, mp 185-186.5°.

Only a few partially boranated polyamine bases are known, however. Tetramethylethylenediamine-borane (TMEN · BH_3) is *not* stable above −1° and disproportionates to TMEN and TMEN · $2BH_3$.[7] The analogous triethylenediamine (TEDA) monoborane adduct was precipitated from an equimolar mixture of TMEN and TEDA · $2BH_3$ after heating to 70° and cooling. This monoadduct is sufficiently stable to be sublimed without purification.

Results and Discussion

Direct combination of hexamine and diborane at slightly greater than 2:1 mol ratio in benzene at 50° gives excellent yield (94%) of the monoadduct. This adduct is amazingly insoluble in all commonly available solvents. It was purified from traces of reactants and other adducts by long stirring in water.

The completely boranated adduct was sought initially in tetrahydrofuran solvent, but the product is analytically impure and very hazardous to handle, enflaming on prolonged contact with air (and one time in a capped vial). Similar experience was encountered with glyme (ethylene glycol dimethyl ether) and diethyl ether. Solvent incorporation, possibly by ether cleavage, seems to have occurred; consequently, a solvent free of oxygen was sought. Surprisingly, benzene was found to serve well, even though it is not commonly used in borane-adduct formation and it is not a good solvent for hexamine and the monoborane adduct. The monoadduct is first formed by addition of one-fourth the required borane and heating to 50° for 2 hr. (There is no reaction without heating.) The remaining diborane is added at room temperature and the result is an apparent solution of the tetraadduct, $(CH_2)_6N_4 \cdot 4BH_3$. All attempts to

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transfer the "solution" led to precipitation; consequently, there is serious question about the solubility of the tetraadduct. The adduct is isolated as a white solid by evaporation of solvent under vacuum.

The triadduct, $(CH_2)_6N_4 \cdot 3BH_3$, is obtained by pumping on the tetraadduct while heating from 35 to 120°. Heating only at 35° gives a product containing 70% triadduct and 30% tetraadduct. Attempts to prepare this adduct by equilibration of equimolar amounts of di- and tetraadducts resulted in mixtures of three adducts which could not be separated.

The water-insoluble diadduct obtained by hydrolysis of the tetraadduct at room temperature can be recrystallized from *N,N*-dimethylformamide.

The syntheses routes are summarized (stoichiometry of hydrolysis was not experimentally confirmed

$$^1/_2B_2H_6 + (CH_2)_6N_4 \xrightarrow[C_6H_6]{50°} (CH_2)_6N_4 \cdot BH_3 \xrightarrow{^3/_2B_6H_6} (CH_2)_6N_4 \cdot 4BH_3$$

$$(CH_2)_6N_4 \cdot 4BH_3 \begin{array}{l} \xrightarrow{\Delta} (CH_2)_6N_4 \cdot 3BH_3 + 5B_2H_6 \\ \xrightarrow[6H_2O]{} (CH_2)_6N_4 \cdot 2BH_3 + 6H_2 + 2H_2BO_3 \end{array}$$

The four borane adducts of hexamine were thus obtained in nominal yields but in excellent purity for study of chemical and physical properties. The adducts decomposed thermally without melting below 300°, and in this property they differ from linear polyamine polyboranes. All but the tetraadduct could be sublimed under vacuum near 100°. The diadduct and monoadduct sublime unchanged, whereas the triadduct sublimes with formation of a trace of diadduct. High thermal stability of the adducts with slight dissociation in the gas phase is consequently inferred. The expected order of decreasing stability to dissociation is realized: $(CH_2)_6N_4 \cdot BH_3, (CH_2)_6N_4 \cdot 2BH_3 > (CH_2)_6N_4 \cdot 3BH_3 > (CH_2)_6N_4 \cdot 4BH_3$. A temperature-composition curve, Figure 1, for the tetraadduct is markedly different from that for $(CH_2)_6N_4 \cdot 4BF_3$ reported by Burg and Martin.[9] The latter adduct slowly loses boron trifluoride without forming intermediate adducts.

Qualitative hydrolysis studies show a lability series paralleling that of thermal dissociation. The tetraadduct is essentially all converted to triadduct in 1 hr at room temperture, and the triadduct is completely converted to diadduct in another 9 hr. No hydrolysis of the di- or monoadducts was observed (any significant amount of monoadduct produced from the diadduct would be collected in the water-insoluble product owing to its poor solubility). Acidic hydrolysis of the monoadduct, however, is rapid and produces the starting amine, hexamine. Because there is no common solvent for all four adducts, more quantitative comparisons were not attempted.

Infrared spectral data for BH and CH stretching frequencies support gradual electron withdrawal from boron as well as methylene carbon on successive dative bonding of BH_3 in the adduct series. The BH frequency increases are shown in Table I. The trend is interpreted as reflecting a decrease in charge transfer to *each* boron as more boranes are attached, with consonant loss of basicity in the uncomplexed nitrogen sites in the adducts. A similar increase of BH frequency with basicity decrease has been reported by Rice, *et al.*[10] They found both symmetrical and asymmetrical stretches increased as basicity of parent base decreased in a series of adducts ranging from trimethylamine-borane to diethyl ether-borane.

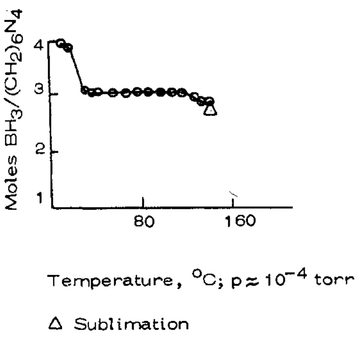

Figure 1.

Table I. BH Frequencies (cm^{-1})

$(CH_2)_6N_4 \cdot BH_3$	$(CH_2)_6N_4 \cdot 2BH_3$	$(CH_2)_6N_4 \cdot 3BH_3$	$(CH_2)_6N_4 \cdot 4BH_3$
	Asymmetrical		
2374 s	2380 s	2394 s	2424 s
	2350 vw, sh		
2324 m	2330 w	2350 w	2368 w
			2344 vw, sh
	Symmetrical		
2280 s	2292 m	2300 m	2314 m

The high frequency CH stretch of the hexamine adducts showed the same trend as the BH stretch, going from 2990 cm^{-1} for monoadduct, to 3001 cm^{-1} for diadduct, to 3030-3040 cm^{-1} doublet for triadduct, and to 3040 cm^{-1} for tetraadduct. Again enhanced electron withdrawal leads to enhanced stretching frequency; this is the generally accepted trend for methyl groups with remote polar substituents.[11]

Previous demonstration of electron withdrawal by boron substituent enhancing stretching frequencies of remote CH bonds may be found in work by Banister, *et al.*[12] The high frequency stretches for the series $(CH_3)_2NBI_2$, $(CH_3)_2NBBr_2$, $(CH_3)_2NBCl_2$, and $(CH_3)_2NBF_2$ are 3017, 3027, 3030, and 3000 cm^{-1}, respectively. It may be assumed that in this series steric effects do not dominate and that the boron unsaturation is primarily satisfied by π-bonding with nitrogen p electrons for all but the fluorine compound (which probably also has considerable halogen back conjugation). Then electron withdrawal should follow halogen electronegativity, increasing from iodine through chlorine, the same order of increasing remote CH stretching frequency.

Structural correlations from nmr studies were limited to the bis- and trisadducts; no solvent could be found for the monoadduct, and benzene "solutions" of the tetraadduct could not be transferred from the reaction flask to nmr tubes without solid appearing. The diadduct had two methylene resonances in 5:1 ratio at 4.64 and 4.38 ppm downfield from tetramethylsilane, and the triadduct had two equivalent resonances at 4.42 and 4.32 ppm. There should be three methylene environments in the diadduct with 1:4:1 population, but it is conceivable that the single N-C-N and the four N-C-N-B environments (see Table II) are coincident. Resonances of the triadduct are assignable to NCNB and BNCNB environments, respectively. The upfield position for the methylene protons compared to the free amine protons (4.69 ppm) is anomalous, as borane complexation ordinarily causes a downfield shift. A diamagnetic shield from

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[9] A. B. Burg and L. L. Martin, *J. Amer. Chem. Soc.*, 65, 1635 (1943).

[10] B. Rice, R. J. Galiano, and W. J. Lehman, *J. Phys. Chem.*, 61, 1222 (1957).

[11] L. J. Bellamy, "Advances in Infrared Group Frequencies," Methuen, New York, N. Y., 1968, p 6.

[12] A. J. Banister, N. N. Greenwood, B. P. Straughan, and J. Walker, *J. Chem. Soc.*, 995 (1964).

Table II. Methylene Environmental Populations in Hexamine-Boranes

	NCH_2N	NCH_2-NBH_3	H_3BNCH_2-NBH_3
$(CH_2)_6N_4$	6		
$(CH_2)_6N_4 \cdot BH_3$	3	3	
$(CH_2)_6N_4 \cdot 2BH_3$	1	4	1
$(CH_2)_6N_4 \cdot 3BH_3$		3	3
$(CH_2)_6N_4 \cdot 4BH_3$			6

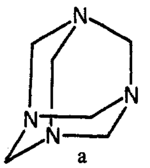
the adjacent BH_3^- hydride umbrellas may be more important than the electron drift effect of the σ framework.

Taken together, the physical data support structures which are simple dative-bonded borane adducts (no evidence for bridge hydrogen). Chemical data, *viz. infra*, show that the borane groups are reversibly bonded and can be removed by thermolysis or displacement by pyridine. The apparent strong bonding of borane in the monoadduct, evidenced by its resistance to displacement with excess pyridine, may be a result of the lattice energy of this adduct (which prevents its solution in any common solvent) rather than an inherently strong B-N bond.

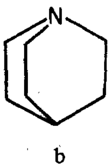
Chemical Properties

Pyrolysis of the tetraadduct in sealed tubes was investigated in search of novel rearrangements. Near 130° the tubes detonated violently. That traces of oxygen or oxygen-containing impurities act as initiators is unlikely since explosions were encountered when all steps were conducted in rigorous vacuum and the adduct transferred to a sealed tube fused to the reaction flask. In tubes which did not explode, trimethylamine, $[(CH_3)_2N]_2BH$, and $[(CH_3)_2NBH_2]_2$ were isolated. The presence of these methylated species can be rationalized by hydride transfer from borane to methylene in the adduct.

Instead of the diversity of cations anticipated from the adducts, by reaction with iodine and subsequent iodide displacement, only one cation was isolated, namely $(CH_2)_6N_4BH_2P(CH_3)_3^+$. Another hexamine-derived cation, $(CH_2)_6N_4BH_2NC_5H_5^+$, was obtained but only by the inverse procedure of adding hexamine to pyridine-iodoborane, so it may be inferred that the transition state during displacement is not symmetrical toward incoming base and the substrate base of the iodoborane. A similar experience in cation formation was reported by Nainan and Ryschkewitsch.[13] These workers were able to prepare $(CH_3)_3NBH_2N(C_2H_5)_3^+$ from $(C_2H_5)_3NBH_2I$ and trimethylamine but not by the inverse procedure. Presumably the large iodine forces the ethyl group into favorable position for reaction to proceed. No such steric effects can be invoked for hexamine-BH_2I, because the "front" of the molecule is cleared by the incorporation of all three nitrogen substituents into chair-form cyclohexane-like rings of the adamantane cage structure of hexamine. A comparison of models of hexamine (a) and quinuclidine (b) reveals almost identical environments about the base sites. The latter amine is known to have less steric hindrance at the nitrogen site than triethylamine,[14] so it may be concluded that hexamine-iodoborane should have less steric requirement than triethylamine-iodoborane. That it *does not* function like triethylamine-iodoborane in the cation synthesis is inexplicable from steric considerations.



a



b

Experimental Section

Materials. Diborane used was commercial grade, used as received from Callery Chemical Co. Between usage the diborane was maintained in a stainless steel cylinder at −78°. Thiophene-free benzene and reagent grade ethyl ether were dried with and stored over sodium wire. Tetrahydrofuran was distilled from lithium aluminum hydride. Triethylamine was distilled and stored over calcium hydride. Pyridine was distilled from and stored over potassium hydroxide. Hexamine, trimethylamine, and *N,N,N′,N′*-tetramethylethylenediamine were commercial samples, used without further purification.

Apparatus. All air-sensitive materials were handled with standard vacuum line techniques in a glass vacuum system equipped with Delmar-Urry valves and O-ring joints. Transfers of nonvolatile, air-sensitive materials were made in a nitrogen-filled polyethylene dry-bag.

Infrared spectra were recorded on a Perkin-Elmer 237B or Beckman IR-10 grating spectrophotometer. Nmr data were obtained with a Varian A-60A.

Chemical analyses were procured from commercial laboratories: Alfred Bernhardt, Elbach, West Germany; Midwest Microlab Inc., Indianapolis; Peninsular ChemResearch, Gainesville, Fla.

Hexamethylenetetramine-Monoborane. A 50% excess, 1.5 g (19.5 mmol), of vacuum-dried hexamine was placed in a 50-ml reaction flask containing a magnetic stirring bar and 30 ml of benzene. The flask was attached to the vacuum system and evacuated with liquid nitrogen cooling. Using the standard vacuum line technique, 4.27 mmol (measured as a gas) of diborane was condensed in. The flask was warmed slowly to room temperature and then to 50°. Stirring was continued at this temperature for 3 hr at which time a flocculent solid was present. Volatiles were removed under vacuum and the white solid residue was washed with water to remove traces of hexamine. After drying, 1.23 g, 85%, of hexamine-BH_3 was obtained.

Anal. Calcd for $(CH_2)_6N_4 \cdot BH_3$: C, 46.8; H, 9.8; N, 36.4; B, 7.0. Found: C, 46.8; H, 9.8; N, 36.2; B, 6.9.

Hexamethylenetetramine-Bisborane. A 1.37-g portion (7.06 mmol) of $(CH_2)_6N_4 \cdot 4BH_3$ was stirred in water for 3 days during which hydrogen was evolved. The insoluble material was collected by filtration and air dried 1.17 g, 86%. Recrystallization from dimethylformamide gave 749 mg of white, crystalline bisborane adduct; $(CH_2)_6N_4 \cdot 2BH_3$.

Anal. Calcd for $(CH_2)_6N_4 \cdot 2BH_3$: C, 42.9; H, 10.8; N, 33.4; B, 12.9. Found: C, 42.7; H, 10.7; N, 32.5; B, 13.4. Found (crude product): C, 42.3; H, 10.1; N, 32.5; B, 11.9.

Hexamethylenetetramine-Trisborane. In a 50-ml flask equipped with stirring bar and serum-capped side arm, 305 mg (2.16 mmol) of hexamine and 20 ml of benzene were treated with excess diborane as described under hexamine-tetrakisborane preparation. Benzene was removed and the product tetraadduct was dried under vacuum. A solution of 426 mg (2.34 mmol) of bisborane adduct in 20 ml of dimethylformamide was added *via* a syringe. The mixture was stirred 10 hr and the solvent was removed under vacuum. The infrared spectrum of the product showed a mixture of bis-, tris-, and tetraadducts.

A pure sample of trisadduct was obtained by heating 650 mg of tetraadduct gradually to 120° maximum. The volatile product collected in an attached trap cooled to −196° was identified as diborane (1.56 mmol) and measured to be (within 5%) $^1/_4$ equivalent of the boron originally taken.

Anal. Calcd for $(CH_2)_6N_4 \cdot 3BH_3$: C, 39.7; H, 11.6; N, 30.8; B, 17.9. Found: C, 39.2; H, 11.1; N, 29.6; B, 16.0. Found (for sample from proportionation experiment): C, 39.6; H, 11.3; N, 30.1.

Hexamethylenetetramine-Tetrakisborane. In a 50-ml round-bottomed flask attached to a vacuum line (*via* an O-ring joint) and equipped with a stirring bar were placed 493 mg (3.48 mmol) of $(CH_2)_6N_4$ and 30 ml of dry benzene. After cooling to −196°, 1.74 mmol of diborane was introduced and the mixture allowed to warm to room temperature. Then the mixture was slowly heated to 50° and stirred for 3 hr at which time a white flocculent precipitate of the monoadduct is present (identified by infrared spectrum). The mixture was again cooled and another 5.22 mmol of diborane added. On warming and stirring at room temperature, formation of the tetraadduct was evidenced by a "dissolution" (by appearance) of the solid. After 10 hr the flask was cooled to −78°, and excess di-

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borane was removed under vacuum. Benzene was removed at room temperature to leave while solid tetraadduct (96%) which was handled under nitrogen because of its extreme sensitivity to moisture and air. Identification was based on infrared spectrum, preparative stoichiometry (3.48 mmol of hexamine to 13.38 mmol of BH_3 consumed, corresponding to a 1:3.85 ratio), and analysis.

Anal. Calcd for $(CH_2)_6N_4 \cdot 4BH_3$: C, 36.9; H, 12.4; N, 28.7; B, 22.1. Found: C, 38.3, 38.9; H, 11.8, 11.0; N, 29.6, 29.0; B, 21.4.

The tetraadduct slowly decomposes to the triadduct and diborane even at room temperature in sealed ampoules, which fact accounts for the high CH and low B values.

Borane Removal with Pyridine. A white viscous mixture of 10 ml of pyridine and 900 mg (4.58 mmol) of tetraadduct was stirred overnight at room temperature. The solid was filtered, washed with pyridine, and identified as monoadduct, 656 mg, 90%. The filtrate was freed of pyridine by heating at 50° under high vacuum for 2 hr to leave 889 mg of pyridine–borane, 94% yield based on boron charged.

$H_2BP(CH_3)_3N_4(CH_2)_6^+$ Salts. A 3.62-mmol sample of hexamine-borane was monoiodinated in 10 ml of chloroform by slow addition, with stirring, of 408 mg (1.61 mmol) of iodine in 20 ml of chloroform. A 10% excess of trimethylphosphine was condensed into the flask under vacuum, and the resulting mixture was stirred 3 hr at room temperature. Solvent was removed under vacuum and the remaining (iodide salt) solid was dissolved in 5 ml of warm water and treated with excess $NH_4^+PF_6^-$ solution. The white precipitate was collected and recrystallized from 50° water to give 143 mg of $(CH_2)_6N_4BH_2P(CH_3)_3^+PF_6^-$.

Anal. Calcd for $(CH_2)_6N_4BH_2P(CH_3)_3^+PF_6^-$: C, 28.9; H, 6.2; N, 15.0; B, 2.9. Found: C, 27.9; H, 5.9; N, 13.0; B, 2.5.

$H_2BpyN_4(CH_2)_6^+$ Salts. A combination of hexamine–BH_2I solution in chloroform or benzene (prepared as described) with pyridine gave no isolable cation salt. The reverse combination of excess hexamine with 257 mmol of py–BH_2I (prepared from 2.57 mmol of py–BH_3 and 163.1 mg of iodine) in benzene resulted in a slow deposition of white solid product which was separated by filtration. This product was dissolved in hot water and treated with ammonium hexafluorophosphate solution, whereupon the slightly soluble hexafluorophosphate salt precipitated. It was collected by filtration quickly to minimize decomposition.

Anal. Calcd for $BH_2pyN_4(CH_2)_6^+PF_6^-$: C, 35.0; H, 5.1; N, 18.6. Found: C, 34.8; H, 4.3; N, 16.6.

Pyrolysis of Tetraadduct. A 3.5-mmol sample of tetraadduct was prepared in a 50-ml flask attached to a vacuum line. Benzene solvent was removed under vacuum and the flask sealed off at a constriction and placed in an oil bath behind safety shielding. Pyrolysis was carried out by heating at 110° for 10 hr, 130° for 24 hr, and 140° for 2 hr. A clear liquid and white and yellow solids were present at this time. After cooling to room temperature the flask was opened and 6.77 mmol of noncondensable gas (H_2 ?) was separated from condensable material fractionated through −40°, −78°, and −196° traps. Trimethylamine (0.349 mmol) collected in the −196° trap, and $[(CH_3)_2N]_2BH$ as a clear liquid and $[(CH_3)_2NBH_2]_2$ as a white solid collected in the −78 and −40° traps, respectively. Identification was made by gas density molecular weight measurements and infrared data. The measured molecular weight of the liquid was 97 (17.13 mg, 19.74 mm, 167.1 ml, 24.8°) compared with the theoretical 99.8, and the measured molecular weight of the solid was 117 (8.70 mg, 8.29 mm, 166.8 ml, 24.2°) compared with the theoretical 113.6. Infrared spectra were similar to those reported for these compounds.[15] These borane compounds accounted for 47% of the boron charged. Treatment of the nonvolatile residue with warm methanol gave some insoluble monoborane hexamine adduct and a solution containing material which could not be characterized.

Acknowledgment. Support of this research by a grant from the National Science Foundation is gratefully acknowledged.

Registry No. $(CH_2)_6N_4 \cdot BH_3$, 14547-02-5; $(CH_2)_6N_4 \cdot 2BH_3$, 42976-00-1; $(CH_2)_6N_4 \cdot 3BH_3$, 42976-01-2; $(CH_2)_6N_4 \cdot 4BH_3$, 42976-02-3; $(CH_2)_6N_4$, 100-97-0; B_2H_6, 19287-45-7; $(CH_2)_6N_4BH_2P(CH_3)_3$-PF_6^-, 42934-44-1; $BH_2pyN_4(CH_2)_6^+PF_6^-$, 42934-45-2.

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Ab Initio Self-Consistent-Field Study of Boron Halides: B_4F_4 and B_4Cl_4

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Received August 1, 1973

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.

I. Introduction

The electronic structures of certain boron halides have been of interest for many years. In particular, the molecules studied most extensively by experimental and both semiempirical and *ab initio* theoretical methods have been the trigonally bonded boron halides BX_3 (X = F, Cl, Br, or I).[1-6] Also, there have been several approximate self-consistent-field (SCF) and extended Huckel (EH) studies of B_2Cl_4[1] and B_4Cl_4.[6,7] The bonding in these molecules is of particular interest because of the possibility of back-coordination from the halides to vacant p orbitals on the borons.[8,9] For in-

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