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## Reactions of N-Trimethylborazine with Anhydrous Hydrogen Halides

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N-Trimethylborazine undergoes reversible addition reactions with hydrogen halides to form compounds of the empirical formula (CH<sub>3</sub>)<sub>3</sub>N<sub>3</sub>B<sub>3</sub>H<sub>3</sub>·3HX. At elevated temperatures, hydrogen-halogen exchange occurs to yield B-halogenated derivatives of N-trimethylborazine and hydrogen. Bromine reacts under equivalent conditions to yield the previously unreported N-trimethyl-B-dibromoborazine. Hydrogen bromide forms a 3:1 adduct with B-trichloroborazine but the analogous reaction between hydrogen chloride and B-tribromoborazine could not be effected. The infrared spectra of the hydrogen halide adducts were recorded in the 4000-650-cm<sup>-1</sup> region and partial assignments are proposed.

### Introduction

The reactions of N-trimethylborazine with heavy-metal halides yield unsymmetrically B-substituted haloborazines;<sup>1-3</sup> secondary products arise from the liberated hydrogen halide and the starting borazine. Although the addition reactions between hydrogen halides and borazines are well-known,<sup>4,5</sup> the hydrogen halide adducts of N-trimethylborazine have not been characterized. Moreover the reactions between hydrogen halides and borazines under the conditions necessary to effect reaction between heavy-metal halides and N-trimethylborazine<sup>2,3</sup> have not been investigated. We report here the preparation of the hydrogen halide adducts of N-trimethylborazine, the results of pyrolyzing these adducts under varied conditions, and an investigation of the reaction between N-trimethylborazine and bromine. In addition an interpretation is given of the infrared spectra of the hydrogen halide

adducts of N-trimethylborazine and the hydrogen bromide adduct of B-trichloroborazine.

### Experimental Section

Standard methods of syntheses were employed for the preparation of N-trimethylborazine,<sup>6</sup> B-tribromoborazine,<sup>7</sup> and B-trichloroborazine.<sup>8</sup>

Hydrogen iodide was generated by the reaction of sodium iodide with 85% phosphoric acid at 150°;<sup>9</sup> the resulting hydrogen iodide was swept in a stream of dry nitrogen through a trap at -23° and a phosphorus pentoxide drying tower.

Bromine (reagent grade, Mallinckrodt) was stored over pulverized potassium bromide for approximately 6 months and distilled into a trap maintained at -196° immediately prior to use.<sup>10</sup> Hydrogen bromide (99.8%, Matheson) and hydrogen chloride (technical grade, Matheson) were passed through phosphorus pentoxide drying towers. Benzene and hexane were distilled after refluxing for several hours over sodium.

**Addition of Hydrogen Halides to *N*-Trimethylborazine.** Addition reactions between the hydrogen halides and *N*-trimethylborazine occurred both in benzene solution at room temperature and with the pure compounds at low temperatures.

For reactions utilizing a solvent, the reaction vessel<sup>11</sup> was fitted with a gas bubbler entry tube and a filter frit; the exit stopcock terminated at a mercury bubbler. After charging the flask with *N*-trimethylborazine (4.35 g, 35 mmol) and benzene (35 ml), the hydrogen halide was bubbled through the magnetically stirred solution until precipitation of the product appeared complete. Generally, the reaction required 1.5–2 hr before the precipitate began to form, after which time it was completed in an additional 10 min. The reaction mixture was filtered and washed with benzene and/or hexane. Residual solvent was removed by evacuation at room temperature for 4–6 hr.

Reactions without a solvent required a reaction flask fitted with a 2-mm straight-bore stopcock. After condensing the hydrogen halide (10 ml) at low temperatures (–97° for HCl, –78° for HBr and HI) in the reaction flask, *N*-trimethylborazine (4.35 g, 35 mmol) was introduced with a syringe through the stopcock. The mixture was warmed to room temperature and after 2 hr unreacted starting materials were removed by evacuating the flask for 4–6 hr at room temperature.

The infrared spectra of the products obtained in these two ways were identical, but elemental analysis indicated that the products found in the absence of a solvent were of higher purity.

*Anal.* Calcd for (CH<sub>3</sub>)<sub>3</sub>N<sub>3</sub>B<sub>3</sub>H<sub>3</sub>·3HCl: B, 13.98; N, 18.12; Cl, 45.90. Found (neat): B, 13.93; N, 18.13; Cl, 45.27; 45.5% yield. Found (solvent): B, 13.61; N, 17.16; Cl, 45.87; 29.2% yield. Calcd for (CH<sub>3</sub>)<sub>3</sub>N<sub>3</sub>B<sub>3</sub>H<sub>3</sub>·3HBr: B, 8.87; N, 11.70; Br, 65.65. Found (neat): B, 9.20; N, 11.66; Br, 65.43; 56.7% yield. Found (solvent): B, 7.90; N, 10.03; Br, 68.37; 48.2% yield. Calcd for (CH<sub>3</sub>)<sub>3</sub>N<sub>3</sub>B<sub>3</sub>H<sub>3</sub>·3HI: B, 6.40; N, 8.30; I, 75.22. Found (neat): B, 6.58; N, 8.27; I, 74.70; 25.0% yield. Found (solvent): B, 6.40; N, 8.05; I, 81.60; 32.1% yield.

**Addition of Hydrogen Bromide to *B*-Trichloroborazine.** An excess of hydrogen bromide was condensed onto *B*-trichloroborazine (2.0 g, 10.9 mmol) in a small reaction vessel maintained at –78°. The slurry was stirred magnetically for 1 hr before allowing excess hydrogen bromide to distill off. Traces of hydrogen bromide were removed from the product, H<sub>3</sub>N<sub>3</sub>B<sub>3</sub>Cl<sub>3</sub>·3HBr, by 2 hr of evacuation at room temperature.

**Attempted Addition of Hydrogen Chloride to *B*-Tribromoborazine.** An excess of hydrogen chloride was condensed onto *B*-tribromoborazine (1.0 g, 3.2 mmol) in a small reaction vessel maintained at –97°. The slurry was stirred for 0.5 hr before excess hydrogen chloride was removed by distillation. The condensation, stirring, and distillation procedure was repeated three times. After 2 hr of final evacuation, the solid was shown to consist of only unreacted *B*-tribromoborazine by its infrared<sup>12</sup> and mass spectra.

Similarly, *B*-tribromoborazine (1.0 g, 3.2 mmol) in benzene (ca. 35 ml) did not react with hydrogen chloride bubbled through the solution for 12.5 hr.

**Pyrolysis Studies.** Samples of (CH<sub>3</sub>)<sub>3</sub>N<sub>3</sub>B<sub>3</sub>H<sub>3</sub>·3HCl, (CH<sub>3</sub>)<sub>3</sub>N<sub>3</sub>B<sub>3</sub>H<sub>3</sub>·3HBr, (CH<sub>3</sub>)<sub>3</sub>N<sub>3</sub>B<sub>3</sub>H<sub>3</sub>·3HI, and H<sub>3</sub>N<sub>3</sub>B<sub>3</sub>Cl<sub>3</sub>·3HBr were pyrolyzed in a mass spectrometer oven. The mass spectrum in each case consisted only of mass peaks characteristic of the uncomplexed borazine and the corresponding hydrogen halides. There was no evidence for the halogenation or transhalogenation of the borazine nucleus.

Samples of (CH<sub>3</sub>)<sub>3</sub>N<sub>3</sub>B<sub>3</sub>H<sub>3</sub>·3HCl and (CH<sub>3</sub>)<sub>3</sub>N<sub>3</sub>B<sub>3</sub>H<sub>3</sub>·3HBr were heated in vacuo to 110° and the products passed through traps maintained at –78 and –196°. *N*-Trimethylborazine and the corresponding hydrogen halide were isolated in the respective traps and identified by their infrared spectra.<sup>13,14</sup>

(CH<sub>3</sub>)<sub>3</sub>N<sub>3</sub>B<sub>3</sub>H<sub>3</sub>·3HCl (1.0 g, 4.3 mmol) was heated in a sealed tube at 165° for 24 hr. Hydrogen was formed in the reaction; hydrogen chloride was absent. Vacuum-line fractionation of the reaction mixture through traps maintained at –10, –23, and –196° yielded impure *N*-trimethyl-*B*-dichloroborazine (0.24 g, 1.3 mmol; 29.3%) in the –10° trap; mp 94–104°; lit.<sup>3</sup> mp 99–99.5°. The residue (0.50 g) was shown to be a mixture of *N*-trimethyl-*B*-dichloroborazine and *N*-trimethyl-*B*-trichloroborazine by its infrared and mass spectra.

The reaction of (CH<sub>3</sub>)<sub>3</sub>N<sub>3</sub>B<sub>3</sub>H<sub>3</sub>·3HBr under identical conditions gave essentially the same results.

**Reaction of *N*-Trimethylborazine with H<sub>3</sub>B<sub>3</sub>N<sub>3</sub>(CH<sub>3</sub>)<sub>3</sub>·3HCl.** *N*-Trimethylborazine (1.04 g, 8.5 mmol) and the hydrogen chloride

adduct of *N*-trimethylborazine (1.0 g, 4.3 mmol) were heated at 165° for 24 hr in a sealed tube. Vacuum-line fractionation of the products through traps maintained at –10, –23, and –196° gave a fraction containing mostly *N*-trimethyl-*B*-chloroborazine (mass spectra) in the –10° trap (1.12 g, 7.15 mmol; 55.8%) and in the –23° trap (0.20 g, 1.27 mmol; 9.9%). Unreacted *N*-trimethylborazine (0.34 g, 2.76 mmol; 21.6%) was recovered from the –196° trap.

**Reaction of *N*-Trimethylborazine with Bromine.** *N*-Trimethylborazine (1.16 g, 9.45 mmol) and bromine (1.51 g, 9.48 mmol) were heated at 165° for 24 hr in a sealed tube. The gaseous product was hydrogen. *N*-Trimethyl-*B*-dibromoborazine (1.25 g, 4.45 mmol; 47.1%) was sublimed in vacuo from the solid residue at 37° and was purified by sublimation in a gradient furnace,<sup>11</sup> mp 73–77°. The product was characterized by its mass spectrum which showed only mass peaks of the parent ion (*m*) and the ion arising from the loss of a hydrogen atom (*m* – 1).

**Infrared Spectra.** The infrared spectrum of H<sub>3</sub>B<sub>3</sub>N<sub>3</sub>(CH<sub>3</sub>)<sub>3</sub>·3HCl was recorded in a KBr pellet; the spectra of the other cycloborazane derivatives are reported as composites of Nujol and hexachlorobutadiene mulls. The mulls and pellets were prepared in a helium-filled drybox, the atmosphere of which was equilibrated with the liquid Na–K eutectic. The mass spectrum exhibited the expected distribution of mass peaks expected for the natural isotope composition of the elements present. Infrared spectra were recorded with a Beckman IR-7 infrared spectrophotometer; the results are summarized in Table I.

## Discussion

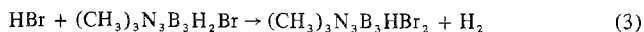
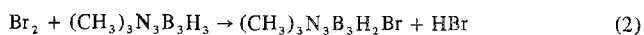
The general reaction of hydrogen halides with *N*-trimethylborazine is expressed by eq 1. At room temperature,

$$3HX + (\text{CH}_3)_3\text{N}_3\text{B}_3\text{H}_3 \rightleftharpoons (\text{CH}_3)_3\text{N}_3\text{B}_3\text{H}_3 \cdot 3HX \quad (1)$$

three molecules of hydrogen halide add to one molecule of *N*-trimethylborazine; at higher temperatures (about 100°) the adduct dissociates and the original hydrogen halide and *N*-trimethylborazine can be recovered. Similar observations on related compounds have been reported.<sup>5,15,16</sup>

At elevated temperatures (about 165°) in a closed system an exchange reaction occurs between hydrogen chloride and *N*-trimethylborazines to yield *B*-chloro-*N*-trimethylborazines and hydrogen. The reaction is similar to that reported for heavy-metal halides and may proceed via a similar intermediate.<sup>2</sup> If equimolar amounts of hydrogen chloride and *N*-trimethylborazine are used, *N*-trimethyl-*B*-chloroborazine can be produced as a primary product of the exchange reaction. The adduct, (CH<sub>3</sub>)<sub>3</sub>N<sub>3</sub>B<sub>3</sub>H<sub>3</sub>·3HCl provides a convenient source of hydrogen chloride for this reaction since it dissociates at elevated temperatures. Thus, a sealed tube reaction of *N*-trimethylborazine and the (CH<sub>3</sub>)<sub>3</sub>N<sub>3</sub>B<sub>3</sub>H<sub>3</sub>·3HCl in a 2:1 mole ratio yielded *N*-trimethyl-*B*-chloroborazine in good yield.

A similar reaction occurs between hydrogen bromide and *N*-trimethylborazine at elevated temperatures. However, the reaction between stoichiometric amounts of bromine and *N*-trimethylborazine is a more convenient synthesis for partially brominated derivatives of *N*-trimethylborazine. The reaction of bromine with *N*-trimethylborazine proceeds in two steps.



The first step (eq 2) occurs at room temperature<sup>17</sup> and is similar in nature to the low-temperature reaction observed with heavy-metal halides.<sup>2</sup> An identical reaction occurs between iodine and *N*-trimethylborazine.<sup>18</sup> The second step (eq 3) occurs under thermal conditions where the adduct formed in eq 2 is dissociated, but the dissociation products are contained so that reaction occurs.

The addition of hydrogen chloride to *B*-tribromoborazine could not be effected although hydrogen bromide readily added to *B*-trichloroborazine under the same conditions. Assuming that the expected products of the two reactions would be either identical or isomers of each other, the inability of hydrogen chloride to form an adduct with *B*-tribromoborazine cannot

**Table I.** Infrared Spectra of the Hydrogen Halide Adducts of *N*-Trimethylborazine and the Hydrogen Bromide Adduct of *B*-Trichloroborazine<sup>a</sup>

| Assignment          | H <sub>3</sub> N <sub>3</sub> B <sub>3</sub> Cl <sub>3</sub> ·3HBr | (CH <sub>3</sub> ) <sub>3</sub> N <sub>3</sub> ·B <sub>3</sub> H <sub>3</sub> ·3HCl | (CH <sub>3</sub> ) <sub>3</sub> N <sub>3</sub> ·B <sub>3</sub> H <sub>3</sub> ·3HBr | (CH <sub>3</sub> ) <sub>3</sub> N <sub>3</sub> ·B <sub>3</sub> H <sub>3</sub> ·3HI |
|---------------------|--|---|---|--|
| ν(N-H)              | 3220 sh, m   | 3225 sh, m  | 3220 m  | 3220 sh, w   |
|                     | 3180 m   | 3220 m  | 3180 m  | 3180 m   |
| ν(CH <sub>3</sub> ) |  | 3030 w  | 3160 m  | 3160 m   |
|                     |  | 2970 w  | 2970 w  | 3060 w   |
|                     |  |   | 2930 w  | 2960 w   |
| ν(B-H)              |  | 2510 sh, m  | 2520 m  | 2520 w   |
|                     | 1544 m   | 2480 m  |   |  |
| δ(CH <sub>3</sub> ) |  | 1475 sh, m  | 1467 m  | 1462 m   |
|                     |  | 1460 m  | 1462 sh, m  | 1454 m   |
|                     |  | 1420 m  | 1422 m  | 1421 m   |
|                     | 1440 m   |   | 1415 sh, m  | 1414 m   |
| ν(B-N)              |  |   | 1370 m  | 1370 w   |
|                     |  |   | 1365 w  |  |
|                     |  | 1343 m  | 1355 m  | 1355 w   |
|                     |  |   | 1338 m  | 1338 w   |
|                     | 1260 vs  | 1265 br, s  | 1258 vs   | 1246 vs  |
|                     | 1230 m   |   | 1235 vs   | 1222 s   |
|                     |  |   | 1175 s  | 1175 m   |
|                     | 1150 w   | 1155 m  | 1155 m  | 1153 m   |
|                     |  | 1140 m  | 1123 m  | 1132 w   |
|                     |  |   | 1118 m  |  |
| ν(B-X)              |  |   | 1100 m  |  |
|                     |  | 1068 w  | 1075 w  | 1080 w   |
|                     |  |   | 1050 m  |  |
|                     |  | 1035 s  | 1038 m  | 1037 s   |
|                     |  | 1020 s  | 1012 s  |  |
|                     |  |   | 1005 s  |  |
|                     | 975 br, s  | 985 m   | 985 s   | 992 s  |
|                     |  |   |   | 971 m  |
|                     |  |   |   | 955 s  |
|                     |  |   | 897 s   | 942 m  |
| γ(B-H)              |  | 888 m   | 885 s   | 882 m  |
|                     |  | 863 m   | 860 m   | 871 m  |
|                     |  | 850 m   | 843 m   | 840 m  |
|                     |  |   |   | 836 m  |
|                     | 813 w  |   |   | 810 sh, w  |
|                     | 807 w  |   | 790 w   | 800 w  |
|                     |  | 765 w   | 775 w   |  |
|                     | 732 w  | 712 m   |   |  |
|                     |  | 693 sh, w   |   |  |
|                     | 640 m  |   |   |  |
|                     | 635 m  |   |   |  |

<sup>a</sup> Symbols: ν, stretch; γ, in-plane bend; δ, out-of-plane bend; w, weak; m, medium; s, strong; v, very; br, broad; sh, shoulder.

be explained by steric arguments. A possible solution to this curious problem lies in the relative basicities of the nitrogen site in the two *B*-haloborazines. On theoretical grounds, it might be expected that boron-halogen π interactions would be more important for B-Cl rather than B-Br moieties. Indeed, structural data on *B*-trichloroborazine<sup>20</sup> indicate that the B-Cl bond distances in this borazine (1.760 ± 0.015 Å) and in BCl<sub>3</sub> (1.74 ± 0.02 Å)<sup>2</sup> are the same within experimental error and are shorter than the sum of the expected single-bond radii (1.87 Å). Although data on the bond distances in *B*-bromoborazines are not available, other results suggest that there would be less π interaction in B-Br-containing compounds than those containing a B-Cl group.<sup>22</sup> The smaller halogen-boron π interaction in *B*-bromoborazines should increase the nitrogen-boron π interaction, making the nitrogen sites less basic in *B*-bromoborazines. This effect together with a greater intrinsic acidity for HBr compared to HCl, differences which should be maximized in hydrocarbon solvents, could lead to the formation of (CH<sub>3</sub>)<sub>3</sub>N<sub>3</sub>B<sub>3</sub>Cl<sub>3</sub>·3HBr under conditions where (CH<sub>3</sub>)<sub>3</sub>N<sub>3</sub>B<sub>3</sub>Br<sub>3</sub>·3HCl would not form.

**Infrared Spectra.** The infrared spectra of the hydrogen bromide adduct of *B*-trichloroborazine and the hydrogen halide adducts of *N*-trimethylborazine are considerably more complex

than the infrared spectra of either *B*-trichloroborazine<sup>12</sup> or *N*-trimethylborazine.<sup>13</sup> Only limited spectral interpretations have been attempted for cyclotriborazanes or related compounds.<sup>5,15,17,19,23</sup>

The strongest absorption bands in the infrared spectra of the cyclotriborazine derivatives prepared in this investigation and those reported<sup>5,17</sup> are observed at about 1260 cm<sup>-1</sup>. These bands are tentatively assigned to boron-nitrogen stretching modes. The displacement of the absorptions from the characteristic frequencies observed for ν(B-N) modes in the infrared spectra of borazine derivatives (ca. 1400 cm<sup>-1</sup>)<sup>24</sup> may be the result of the reduction of the boron-nitrogen bond order.<sup>25</sup>

A significant decrease in frequency is also observed for the nitrogen-hydrogen stretching modes in the cyclotriborazine derivatives.<sup>5,23</sup> These bands, observed at ca. 3200 cm<sup>-1</sup> in the infrared spectra of the cyclotriborazine derivatives, are in the range expected for ammonium ions and are approximately 275 cm<sup>-1</sup> lower than the N-H frequency in the infrared spectra of the corresponding borazines.

The boron-halogen stretching modes in the infrared spectra of the hydrogen halide adducts of *N*-trimethylborazine are observed at frequencies very similar to the corresponding ν(B-X) modes in *N*-trimethyl-*B*-trihaloborazines.<sup>26,27</sup> The ν(B-X) mode in the infrared spectrum of H<sub>3</sub>N<sub>3</sub>B<sub>3</sub>Cl<sub>3</sub>·3HBr yields a very broad absorption at ca. 975 cm<sup>-1</sup>. This frequency is lower than ν(B-X) absorptions in the infrared spectra of the corresponding *B*-trihaloborazines<sup>12</sup> or the hydrogen halide adducts of borazine<sup>5</sup> but intermediate to the strong bands observed at 990 cm<sup>-1</sup> in the infrared spectrum of H<sub>3</sub>N<sub>3</sub>B<sub>3</sub>Cl<sub>3</sub>·3HCl<sup>17</sup> (assigned to ν(B-Cl)) and at 955 cm<sup>-1</sup> in the infrared spectrum of H<sub>3</sub>N<sub>3</sub>B<sub>3</sub>Br<sub>3</sub>·3HBr<sup>17</sup> (ν(B-Br)).

The frequencies of the bands associated with the boron-hydrogen stretching and bending modes and the methyl stretching and bending modes in the compounds (CH<sub>3</sub>)<sub>3</sub>N<sub>3</sub>B<sub>3</sub>H<sub>3</sub>·3HX correspond to those assigned in the infrared spectrum of *N*-trimethylborazine.<sup>13,28</sup> The N-H<sub>2</sub> bending mode in the infrared spectrum of H<sub>3</sub>N<sub>3</sub>B<sub>3</sub>Cl<sub>3</sub>·3HBr corresponds to the bands assigned to this mode in the infrared spectra of related compounds.<sup>17,19,23</sup>

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**Registry No.** (CH<sub>3</sub>)<sub>3</sub>N<sub>3</sub>B<sub>3</sub>H<sub>3</sub>·3HCl, 55156-61-1; (CH<sub>3</sub>)<sub>3</sub>N<sub>3</sub>B<sub>3</sub>H<sub>3</sub>·3HBr, 55156-62-2; (CH<sub>3</sub>)<sub>3</sub>N<sub>3</sub>B<sub>3</sub>H<sub>3</sub>·3HI, 55156-63-3; H<sub>3</sub>N<sub>3</sub>B<sub>3</sub>Cl<sub>3</sub>·3HBr, 55156-64-4; *N*-trimethyl-*B*-dichloroborazine, 13401-08-6; *N*-trimethyl-*B*-chloroborazine, 13401-07-5; *N*-trimethyl-*B*-dibromoborazine, 13401-10-0; *N*-trimethylborazine, 1004-35-9.

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## Use of Pseudopotential Theory to Study Molecular Structure. The Phosphorus Halides

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The theory of *ab initio* pseudopotential SCF methods is applied to the four  $PX_3$  phosphorus halides. The geometries, force constants, orbital energies, Mulliken populations, and dipole moments are calculated using a minimum Slater basis set. Detailed comparisons are made with experiment where possible and, in the case of  $PF_3$ , with a conventional SCF calculation.

### Introduction

There has recently been considerable interest in the use of pseudopotential methods to perform *ab initio* valence-only SCF calculations. We have found in a previous study<sup>1</sup> that the theoretical problems in treating systems with more than one valence electron may be successfully overcome in the case of free atoms and homonuclear diatomic molecules. The present work is the first attempt to extend this method to polyatomic molecules and, in addition to study some of the properties of the pseudo wave functions.

The phosphorus halide series— $PF_3$ ,  $PCl_3$ ,  $PBr_3$ , and  $PI_3$ —is of considerable chemical interest and, with exception of  $PI_3$ , has been extensively studied experimentally. Treating such a series of congeners allows the effect of increasing atomic size of the constituent atoms on molecular properties to be determined. In this paper, we first briefly review the theory and computational methods. The electron distribution of  $PF_3$  as described by a Mulliken population analysis is calculated and compared with conventional SCF results. The calculated equilibrium geometries, force constants, and dipole moments of all four halide molecules are then reported. These are found to be in generally good agreement with the experimental values.

### Method

The object of pseudopotential methods is to replace a conventional Hamiltonian operator, in this case the closed-shell Fock operator

$$F\phi_i = [T + U + \sum_j^{\text{occ}} (2J_j - K_j)]\phi_i \quad (1)$$

where  $i$  and  $j$  represent the set of all occupied orbitals, with a pseudo-Fock operator of the form

$$F'\chi_i = [T + U + \sum_j^{\text{valence}} (2J_j - K_j) + V]\chi_i \quad (2)$$

The  $j$ 's now include only a subset of the occupied orbitals, usually the "valence" orbitals. The remaining occupied orbitals, the "core" orbitals, are not solved for explicitly, but their presence is made known to the valence orbitals through the pseudopotential function  $V$ .  $\chi_i$  is a pseudo wave function that is essentially identical with  $\phi_i$  in the valence region but indeterminate in the core region, that is, near the nuclei. In practice, use of a pseudo wave function to determine molecular properties offers a very great computational advantage, since the basis set used to describe  $\chi_i$  may be much smaller than

a conventional Hartree-Fock calculation would require, and also the pseudopotential  $V$  may be chosen to include only one-electron terms. It has the inherent disadvantages that properties of the wave function near the nuclei cannot be determined nor can one-electron properties which emphasize the importance of integration over the wave function near the nuclei.

There are two contributions to  $V$ : a localized repulsive potential to simulate the electrostatic interaction of the core and valence electrons and a nonlocal potential due to the orthogonality constraints. For the first term we use a model potential function of the form  $\sum_A f(r_A)/r_A$  where  $r_A$  is the distance from nucleus  $A$ . We will further assume that

$$\langle \chi_i^B \left| \frac{f(r_A)}{r_A} \right| \chi_j^C \rangle \begin{cases} = \langle \chi_i^B \left| \frac{(1 - e^{-\alpha_A r_A}) N_c^A}{r_A} \right| \chi_j^C \rangle & \text{for } A = B \text{ or } A = C \\ = \langle \chi_i^B \left| \frac{N_c^A}{r_A} \right| \chi_j^C \rangle & \text{for } A \neq B \text{ and } A \neq C \end{cases} \quad (3)$$

where  $N_c^A$  is the number of core electrons on nucleus  $A$  and  $\alpha_A$  is a parameter determined from atomic calculations. The rationale for using this function has been discussed in an earlier paper.<sup>1</sup> We replace the orthogonality constraint with the Phillips-Kleinman term<sup>2</sup> for each atom

$$\sum_A^{\text{atoms}} \sum_c^{\text{atoms}} \frac{N_c^A}{2} |\phi_c^A\rangle (\epsilon_v - \epsilon_c^A) \langle \phi_c^A| \quad (4)$$

where  $\epsilon_c^A$  and  $\phi_c^A$  are the core eigenvalues and eigenfunctions of the operator  $F$  for atom  $A$ . Finally we invoke the frozen core approximation; i.e., the core parameters  $\alpha_A$ ,  $\epsilon_c^A$ , and  $\phi_c^A$  are taken to be properties of the free atom and independent of the molecular environment.  $\epsilon_v$  is then the lowest valence eigenvalue of eq 2, found iteratively. The pseudopotential (or effective potential)  $V$  is thus the sum of expressions 3 and 4. We refer to this specific embodiment of pseudopotential theory as the NOCOR method, for neglect of core orbitals.

The theoretical problems in using a pseudopotential of this form for many-electron systems are well-known.<sup>3</sup> Nonetheless we have found it to be approximately valid in many cases, particularly for atoms. Determination of the strengths and weaknesses of this approximation, as well as the pseudopo-