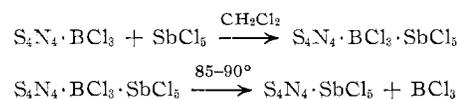


are assigned to  $\nu_3$ ,  $\nu_4$ , and a lattice vibration, respectively. The  $S_4N_4 \cdot SbCl_5$  adduct showed absorptions at 345.5 and 177.5  $cm^{-1}$ , and  $S_4N_4 \cdot BCl_3 \cdot SbCl_5$  showed absorptions at 357 and 181  $cm^{-1}$ . The small differences in the respective Sb-Cl frequencies in all three cases does not allow a choice between formulations B and C for the diadduct. Absorptions in the B-Cl and B-N region slightly favor formulation B, with structure II. Nöth and Lukas<sup>14</sup> have reported B-Cl frequencies at 849 and 842  $cm^{-1}$  and a B-N absorption at 925  $cm^{-1}$ , for  $\{[(CH_3)_2NH]_2BCl_2\}Cl$ . Possibly the peaks at 840 and 932  $cm^{-1}$  of the diadduct correspond to the B-Cl and B-N frequencies, respectively, expected for tetra-valent boron.

The formation of the mixed adduct was surprising (14) H. Nöth and S. Lukas, *Chem. Ber.*, **95**, 1505 (1962).

because diadducts of  $BCl_3$  and  $SbCl_5$  were not formed even though excess  $BCl_3$  and  $SbCl_5$  were present in the preparation of the corresponding monoadducts. Our attempts to form diadducts with  $BCl_3$  and  $SbCl_5$  indicated that, if the diadducts formed at all, they were unstable under the reaction conditions.

Although we were unable to convert  $S_4N_4 \cdot BCl_3$  into  $S_4N_4 \cdot SbCl_5$  directly by treatment with  $SbCl_5$ , this conversion can be effected by the following successive reactions.



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CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING,  
RESEARCH DIVISION, NEW YORK UNIVERSITY, NEW YORK, NEW YORK

## Reactions of Boron Trifluoride with Oxides of Nitrogen

By ASIM B. RAY

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A quantitative study of the reactions between  $BF_3$  and the oxides of nitrogen ( $N_2O_3$ ,  $N_2O_4$ , and  $N_2O_5$ ) was carried out in the absence of solvents. The final products were mixtures of  $B_2O_3$  and  $NOBF_4$  in the case of  $N_2O_3$ , and  $NOBF_4$  and  $O_2$  with  $N_2O_4$  and  $NO_2BF_4$  in the case of  $N_2O_5$ . In the detailed study of the  $N_2O_4$ - $BF_3$  system some of the postulated intermediates were isolated. A mechanism capable of explaining the observations of different authors under divergent conditions is suggested.

The reactions between boron trifluoride and oxides of nitrogen have been the subject of a number of papers.<sup>1-4</sup> Most of these reactions were carried out in the presence of a solvent and below room temperature. The various solid products obtained in these reactions were formulated as  $NO^+$  or  $NO_2^+$  salts of complex boron-containing anions,<sup>1-4</sup> the solids  $BF_3 \cdot N_2O_3$ ,  $BF_3 \cdot N_2O_4$ , and  $BF_3 \cdot N_2O_5$  were regarded,<sup>1-3</sup> respectively, as  $NO^+(BF_3NO_2)^-$ ,  $NO_2^+(BF_3NO_2)^-$ , and  $NO_2^+(BF_3ONO_2)^-$ . Recently<sup>5</sup> it has been shown that the above formulations are erroneous and in reality they are, respectively, mixtures of  $B_2O_3$  and  $NOBF_4$ ,  $B_2O_3$  and various proportions of  $NOBF_4$  and  $NO_2BF_4$  (depending upon reaction conditions), and  $B_2O_3$  and  $NO_2BF_4$ .

Other allied interesting reactions<sup>4,6,7</sup> are those of alkali metal nitrate and nitrite with boron trifluoride in the higher temperature range. Sprague, *et al.*,<sup>4</sup> have carried out the reactions between oxides of nitrogen and  $BF_3$  under various conditions: (a) in the pres-

ence of solvents at low temperatures and (b) in the gaseous phase. They also studied the reactions of  $KNO_3$  and  $NaNO_2$  with  $BF_3$  at elevated temperatures. In all of the above reactions where the same reactants were used they claimed to have obtained identical compounds, *i.e.*,  $NO^+$  or  $NO_2^+$  salts of complex boron-containing species. However, Scott and Shriver<sup>7</sup> have shown (at 180°) that with  $NaNO_3$  the only products obtained were  $NaBF_4$ ,  $NOBF_4$ ,  $B_2O_3$ , and  $O_2$ , while with nitrite the products depending upon reaction conditions were nitric oxide, nitrate,  $B_2O_3$ ,  $NaBF_4$ , and  $NOBF_4$ . In no case were the compounds claimed by Sprague, *et al.*, obtained.

It is also interesting to note that in the methods of preparation of  $NOBF_4$  both  $N_2O_3$ <sup>8,9</sup> and  $N_2O_4$ <sup>10</sup> have been recommended.

We studied the reactions between  $BF_3$  and oxides of nitrogen at room temperature and in the absence of any solvent. Particular attention was given to  $N_2O_4$ . In order to obtain stoichiometry of the reactions, various proportions of the reactants were employed.

The main purpose of this paper is to correlate the

- (1) G. B. Bachman and J. Hokama, *J. Am. Chem. Soc.*, **79**, 4370 (1957).
- (2) G. B. Bachman, H. Feuer, B. R. Bluestein, and C. M. Vogt, *ibid.*, **77**, 6188 (1955).
- (3) G. B. Bachman and J. L. Dever, *ibid.*, **80**, 5871 (1958).
- (4) R. W. Sprague, A. B. Garrett, and H. H. Sisler, *ibid.*, **82**, 1059 (1960).
- (5) J. C. Evans, H. W. Rinn, S. J. Kuhn, and G. A. Olah, *Inorg. Chem.*, **3**, 857 (1964).
- (6) P. Baumgarten and W. Burns, *Ber.*, **72**, 1753 (1939).
- (7) R. N. Scott and D. F. Shriver, *Inorg. Chem.*, **3**, 857 (1964).

- (8) E. Wilke-Dörfurt and G. Balz, *Z. Anorg. Allgem. Chem.*, **159**, 197 (1927).
- (9) E. Wilke-Dörfurt, *Angew. Chem.*, **37**, 712 (1924).
- (10) S. A. Voznesenskii and P. P. Kurski, *J. Gen. Chem. USSR*, **8**, 524 (1938).

observations of the various authors noted above and to postulate a reaction mechanism capable of explaining all of the observed facts.

### Experimental Section

**Materials.**—All the gases were purchased from Matheson (reagent grade).

**Nitric oxide** was purified by passing through a  $-160^\circ$  bath and condensing in a liquid nitrogen bath and pumping.

**Dinitrogen tetroxide** was purified by passing through a  $-45^\circ$  bath and condensing in a  $-95^\circ$  bath.

**Dinitrogen trioxide** was made by mixing calculated quantities of purified NO and  $N_2O_4$  in a glass storage bulb and was checked by analysis.

**Dinitrogen pentoxide** was made by distilling  $KNO_3$  (reagent grade, Baker) with concentrated  $H_2SO_4$  (reagent grade, Baker) and fractionating, and then distilling under vacuum the nitric acid thus obtained with  $P_2O_5$  in a current of ozonized oxygen (dry).

**Boron trifluoride** was purified by passing through a  $-125^\circ$  bath. Infrared spectra of the reactants were checked for purity and found satisfactory.

**Reaction of Boron Trifluoride and Nitric Oxide.**—Various proportions of the reactants were condensed in a glass reactor (200 ml) with a 24/40 female joint and an adapter with a Teflon stopcock (Scientific Glass, JS-4880) with a 24/40 male and ending in a 12/30 male joint. The adapter was joined to the reactor with Py-seal cement. The reactor was then allowed to warm up to room temperature and was kept at this temperature or higher (up to  $80^\circ$ ) for various periods of time, but in no case was a reaction observed. Both of the reactants were quantitatively recovered. When  $BF_3$  and NO were condensed together at liquid nitrogen temperature, an orange color was observed, but the color disappeared at about  $-160^\circ$  and then reappeared on cooling. This observation was similar to that of Finlay.<sup>11</sup>

**Reaction of Boron Trifluoride and Dinitrogen Tetroxide.**—In a typical experiment, boron trifluoride (8 mmoles) and  $N_2O_4$  (10 mmoles) were mixed in the manner noted above and were allowed to warm up to room temperature and then to stand for 24 hr. Formation of a white solid was observed at about room temperature. Gaseous products were then admitted to the vacuum line, condensables were collected at  $-196^\circ$ , and noncondensables were collected by means of a Toeppler pump. After the *PVT* measurements of the fractions, condensables were characterized by infrared and noncondensables by mass spectra. Solid products were identified by taking infrared spectra of the Nujol and Kel-F mulls under proper conditions (drybox under nitrogen atmosphere) and also by chemical means (treating with HCl gas and heating with dry KCl under vacuum).

In order to follow the reaction more closely, the reactants were mixed in a gas cell fitted with NaCl optics.

**Reaction of Boron Trifluoride and Dinitrogen Pentoxide.**—The above procedure was used, but a reaction temperature of  $-10^\circ$  was employed.

**Reaction of Boron Trifluoride and Dinitrogen Trioxide.**—In a typical experiment 4.50 mmoles of NO, 4.50 mmoles of  $NO_2$ , and 7.10 mmoles of  $BF_3$  were used. First NO was condensed in the reactor, and then  $N_2O_4$  (required amount) was condensed on top of it. After a dark blue color developed ( $N_2O_3$ ), the mixture was warmed to room temperature. Brown fumes were observed, but a blue liquid still remained inside the reactor. Then the mixture was again cooled to  $-196^\circ$  and  $BF_3$  was introduced into the reactor. The resulting mixture was warmed to  $-10^\circ$  in a salt-ice bath and a white solid formed inside the reactor. The solid was treated as in the previous experiments.

### Results

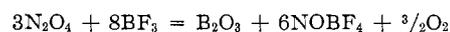
**Dinitrogen Tetroxide.**—When  $N_2O_4$  (in excess) and  $BF_3$  were mixed in a glass reactor, an immediate for-

mation of a white solid was observed. The infrared spectrum of the solid in Nujol and Kel-F mulls on sodium chloride plates gave a spectrum which was consistent with that of a mixture of  $NOBF_4$  and  $B_2O_3$ . In no case did we observe a band due to  $NO_2^+$  (in the  $2380\text{-cm}^{-1}$  region). Since it is well known<sup>4,5</sup> that both  $NOBF_4$  and  $NO_2BF_4$  react with NaCl plates, an independent chemical check was also made. The solid product produced only NOCl when heated under vacuum with dry KCl. With dry hydrogen chloride the solid product gave NOCl,  $BF_3$ , and HF, but no  $NO_2Cl$  was observed.

The mass spectrum of the noncondensable gas produced in the reaction showed the presence of oxygen only. *PVT* measurements showed that for each mole of  $BF_3$  consumed 0.1875 mole of oxygen was evolved.

An infrared spectrum of the condensable gases at the end of the reaction showed only  $NO_2$ .

The over-all reaction consistent with the above observations can be represented as



The similarity of this equation with that proposed by Scott and Shriver<sup>7</sup> for  $NaNO_3$  and  $BF_3$  should be noted.

In order to see whether the reaction between  $N_2O_4$  and  $BF_3$  did proceed through intermediates, the two reactants were mixed in various proportions in a 10-cm gas cell (Perkin-Elmer) fitted with sodium chloride optics.

On mixing the reactants [ $BF_3$  (3 mmoles) and  $N_2O_4$  (0.5 mmole)] in the cell, an immediate white cloud formation was observed, but no brown gas ( $N_2O_4$ ) was found. An immediate spectrum showed  $NO^+$  and  $BF_4^-$  and, in addition, absorptions in the region of a covalent nitrate ( $1625$ ,  $1300$ , and  $840\text{--}860\text{ cm}^{-1}$ ). No NO,  $HNO_3$ , or  $NO_2^+$  band was observed. On standing, the intensities of  $NO^+$  and  $BF_4^-$  bands increased and traces of  $NO_2^+$  band appeared. However, at this point evolution of a brown gas ( $NO_2$ ) was also observed. A similar observation was made when  $N_2O_4$  was in excess ( $N_2O_4:BF_3$  was 2:1) but in this case no  $NO_2^+$  band was observed. (After pumping off the gases from the cell, a spectrum of the cell windows showed absorption in the covalent nitrate region.<sup>12</sup> When the cell was warmed to  $40\text{--}50^\circ$ , a brown gas ( $NO_2$ ) with small amounts of NOCl and  $NO_2Cl$  resulted.) The evolution of  $N_2O_4$  in the above experiment (where  $BF_3$  was in excess) and the absorption in the covalent nitrate region prompted the following experiment.

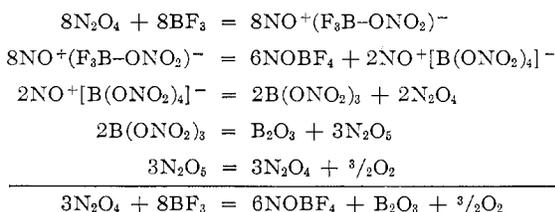
$N_2O_4$  (10 mmoles) and  $BF_3$  (8 mmoles) were condensed in a glass reactor and allowed to stand for 0.5 hr after attaining room temperature. The condensables were fractionated in the vacuum line in the usual manner. The products observed at the various temperatures were:  $-45^\circ$ ,  $N_2O_5$ ;  $-95^\circ$ ,  $N_2O_4$ ;  $-125^\circ$ , an unknown; and  $-196^\circ$ ,  $BF_3$ . The fractions were identified by infrared spectra. The unknown in the  $-125^\circ$  fraction had absorption bands characteristic of  $NO^+$ , a covalent nitrate ( $1625$ ,  $1300$ , and  $840\text{--}860$

(11) G. R. Finlay, *J. Chem. Educ.*, **24**, 149 (1947).

(12) C. R. Guibert and M. D. Marshall, *J. Am. Chem. Soc.*, **88**, 189 (1966).

$\text{cm}^{-1}$ ), and B-F (1490, 1450, and  $710 \text{ cm}^{-1}$ ). Qualitative chemical tests on this fraction showed the presence of boron, fluorine, and nitrogen. On standing, this fraction began to evolve  $\text{NO}_2$ . Although the evidence is inconclusive, it is postulated that the unknown is a mixture of species of the types  $[\text{F}_3\text{B-ONO}_2]^{13}$  and  $[\text{B(ONO}_2)_4]^{12}$ .

From the above observations a probable mechanism for the reaction between  $\text{BF}_3$  and  $\text{N}_2\text{O}_4$  is



**Dinitrogen Trioxide.**—In the literature<sup>1</sup> the product of reaction between boron trifluoride and  $\text{N}_2\text{O}_3$  has been postulated to be  $\text{NO}^+(\text{BF}_3\text{-NO}_2)^-$ . However, Evans, *et al.*,<sup>5</sup> have shown that  $\text{NOBF}_4$  and  $\text{B}_2\text{O}_3$  are the only final products of the reaction between these two reactants. In a typical experiment as described above (where an excess of  $\text{N}_2\text{O}_3$  was employed) the solid product contained  $\text{NOBF}_4$  and  $\text{B}_2\text{O}_3$  only. In the gaseous fraction only  $\text{NO}$  and  $\text{NO}_2$  ( $\text{N}_2\text{O}_3$ ) were found in equal amounts. No noncondensables were present. *PVT* measurements showed that 2.60 mmoles of  $\text{N}_2\text{O}_3$  was consumed for 7.1 mmoles of  $\text{BF}_3$ ; thus the reaction ratio of  $\text{BF}_3$  to  $\text{N}_2\text{O}_3$  was 2.73 and the following equation (identical with the one proposed by Evans<sup>5</sup>) is implied



where the  $\text{BF}_3:\text{N}_2\text{O}_3$  ratio is 2.66.

On treating the solid with excess hydrogen chloride only  $\text{NOCl}$ ,  $\text{BF}_3$ , and  $\text{HF(SiF}_4)$  were obtained.

In another experiment an excess of boron trifluoride was employed. Starting with  $\text{N}_2\text{O}_3$  (2.96 mmoles) and  $\text{BF}_3$  (12.10 mmoles) 4.25 mmoles of  $\text{BF}_3$  was recovered but no  $\text{NO}$  or  $\text{NO}_2$  was found. Thus 7.85 mmoles of  $\text{BF}_3$  reacted with 2.96 mmoles of  $\text{N}_2\text{O}_3$  and the ratio of  $\text{BF}_3$  to  $\text{N}_2\text{O}_3$  was 2.65. The solid product contained only  $\text{NOBF}_4$  and  $\text{B}_2\text{O}_3$ . Thus, the above equation is implied for the reaction between  $\text{BF}_3$  and  $\text{N}_2\text{O}_3$ .

On carrying the reaction above  $-10^\circ$  (room temperature) oxygen was evolved showing that at this temperature  $\text{N}_2\text{O}_4$  was the reactant.

**Dinitrogen Pentoxide.**—The reaction<sup>3</sup> between  $\text{BF}_3$  and  $\text{N}_2\text{O}_5$  produced a solid which has been shown by Evans, Rinn, Kuhn, and Olah<sup>5</sup> to be a mixture of  $\text{NO}_2\text{BF}_4$  and  $\text{B}_2\text{O}_3$ . In a typical experiment 2.1 mmoles of  $\text{N}_2\text{O}_5$  and 6 mmoles of  $\text{BF}_3$  were condensed together in a glass reactor and allowed to stand in a  $-10^\circ$  bath for 1 hr. After this period the gaseous phase contained 0.38 mmole of  $\text{BF}_3$  and traces of oxygen. Thus the amount of  $\text{BF}_3$  consumed was 5.62 mmoles and the ratio of  $\text{BF}_3$  to  $\text{N}_2\text{O}_5$  was 2.67. The solid product gave an infrared spectrum consistent with a mixture of  $\text{NO}_2\text{BF}_4$  and  $\text{B}_2\text{O}_3$ . Small amounts of  $\text{NOBF}_4$  were also

observed. On treating the solid with dry  $\text{KCl}$ ,  $\text{NO}_2\text{Cl}$ , and small amounts of  $\text{NOCl}$  were obtained. The presence of  $\text{NOBF}_4$  and oxygen was probably due to some decomposition<sup>5</sup> of  $\text{N}_2\text{O}_5$  into  $\text{N}_2\text{O}_4$  and  $\text{O}_2$  and subsequent reaction of  $\text{N}_2\text{O}_4$  with  $\text{BF}_3$ . The amounts of oxygen and  $\text{NOBF}_4$  increased with the rise of reaction temperature as would be expected if the source of the decomposition products were  $\text{N}_2\text{O}_5$ .

An equation consistent with the facts is

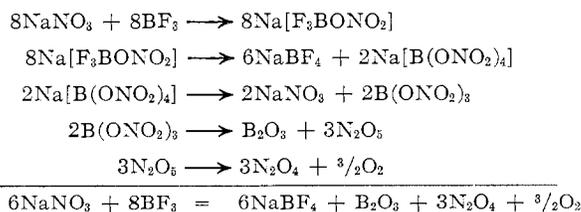


### Discussion

Except for the reaction with  $\text{N}_2\text{O}_4$  our results are substantially in agreement with those of Olah and co-workers.<sup>5</sup> The result of the  $\text{N}_2\text{O}_4$  reaction agreed with that proposed for  $\text{NaNO}_3$  and  $\text{BF}_3$  by Scott and Shriver.<sup>7</sup> The apparent discrepancy in the  $\text{N}_2\text{O}_4$  reaction can be explained by the fact that  $\text{N}_2\text{O}_5$  is one of the intermediates in the reaction and the products obtained will depend upon its behavior. In the method employed by Olah and co-workers it is evident that the formation of  $\text{NO}_2\text{BF}_4$  resulted from the reaction of  $\text{N}_2\text{O}_5$  with  $\text{BF}_3$ . Because of the fact that  $\text{N}_2\text{O}_5$  decomposes<sup>14</sup> appreciably above  $0^\circ$  and in the presence of light and organic impurities, the formation of  $\text{NO}_2\text{BF}_4$  will be a function not only of temperature but also of the purity of the reactants and the manner in which the reaction is performed.

Note that when  $\text{BF}_3$  was in excess in our experiments with  $\text{N}_2\text{O}_4$ , evidence for the presence of  $\text{NO}_2^+$  band was found. It is obvious from the mechanism proposed for  $\text{N}_2\text{O}_4$  and  $\text{BF}_3$  that the formation of  $\text{NO}_2\text{BF}_4$  will take place along with  $\text{NOBF}_4$  if proper conditions such as lower temperature, solvent to prevent decomposition of  $\text{N}_2\text{O}_5$ , and an excess of  $\text{BF}_3$  are employed. Evans' finding that  $\text{NO}^+$  and  $\text{NO}_2^+$  tetrafluoroborates were formed in different ratios depending upon reaction conditions can be explained by the different amounts of  $\text{N}_2\text{O}_5$  decomposing under the prevalent conditions.

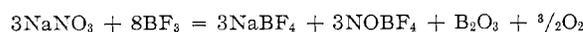
On the basis of the above proposed mechanism the reaction between  $\text{BF}_3$  and  $\text{NaNO}_3$  proposed by Scott and Shriver<sup>7</sup> can be explained as



and



adding and dividing we have



The above equation is identical with the one proposed by Scott and Shriver.

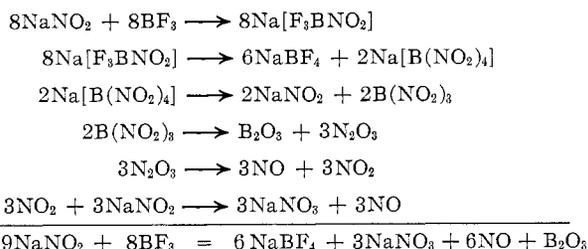
In the above scheme some of the intermediates,

(13) J. Weidlein and K. Dehnicke, *Chem. Ber.*, **98**, 3053 (1965).

(14) N. V. Sidgwick in "Chemical Elements and their Compounds," Vol. 1, Oxford University Press, London, 1950, p. 691.

such as  $[B(ONO_2)_4]^-$ , should be isolable in view of recent work.<sup>12</sup> We did find that when  $(CH_3)_4NNO_3$  is treated with  $BF_3$  at room temperature for 0.5 hr and then the excess  $BF_3$  is pumped off, the solid gave a spectrum (Irtran plates) which had absorptions in the covalent nitrate region<sup>12</sup> (1582–1626 and 1297–1311  $cm^{-1}$ ).

Similarly, the reaction between  $NaNO_2$  and  $BF_3$ , where the amount of  $BF_3$  is less than the stoichiometric quantity, can be visualized as taking place in the following manner



The above equation is identical with the one proposed

by Scott and Shriver for the above reaction conditions.

Scott and Shriver obtained  $NOBF_4$ ,  $NO$ ,  $NaBF_4$ , and small amounts of a noncondensable (not identified) when  $BF_3$  (excess) reacted with  $NaNO_2$  (heated to  $180^\circ$ ). In this reaction the quantities of the individual gaseous products were not given. This observation can also be explained by the reaction scheme for nitrite (where it was in excess). In this case after the decomposition of  $N_2O_3$  into  $NO$  and  $NO_2$ , the  $NO_2$  will react with  $BF_3$  forming  $NOBF_4$ ,  $B_2O_3$ , and  $O_2$  according to the equation proposed for the reaction between  $N_2O_4$  and  $BF_3$ . It can be seen easily that all of the  $NO$  formed in the decomposition of  $N_2O_3$  will not be converted into  $NO_2$  as sufficient oxygen is not available. Hence, a trace of oxygen together with  $NO$  (major) will be the only gaseous products of this reaction.

**Acknowledgment.**—The author wishes to express his appreciation to Professor L. Dauerman for his encouragement and support during the progress of this work.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,  
HARVARD UNIVERSITY, CAMBRIDGE, MASSACHUSETTS 02138

## Molecular and Crystal Structure of $B_7C_2H_{11}(CH_3)_2$

BY DONALD VOET AND WILLIAM N. LIPSCOMB

Received August 26, 1966

A three-dimensional X-ray diffraction study has yielded a structure of  $C_3$  symmetry for  $B_7C_2H_{11}(CH_3)_2$  in which the  $B_7C_2$  unit is an icosahedral fragment. In the open face of this fragment there are two adjacent bridge H atoms and two  $CH(CH_3)$  groups, as was suggested from chemical and spectroscopic studies. Molecular orbital studies of the analogous  $B_7C_2H_{13}$  molecule suggest that axial methylene hydrogen atoms are more positive than equatorial methylene hydrogen atoms. There are four molecules of  $B_7C_2H_{11}(CH_3)_2$  in a unit cell having parameters  $a = 10.56$ ,  $b = 17.35$ ,  $c = 5.57$  Å, and  $\beta = 82.4^\circ$ . The space group is  $P2_1/n$ , and the value of  $R = \sum |F_o| - |F_c| / \sum |F_o|$  is 0.08 for the 1146 observed reflections.

The compound  $B_7C_2H_{13}$  is produced<sup>1</sup> by oxidation of  $B_9C_2H_{11}$  by  $K_2Cr_2O_7$  in acetic acid solution. Spectroscopic and chemical evidence suggests<sup>1</sup> that there are two bridge H atoms and two  $CH_2$  groups. In the  $C, C'$ -dimethyl derivative,  $B_7C_2H_{11}(CH_3)_2$ , easily exchanged BHB bridges and  $CH'$  units have been identified by Tebbe, Garrett, and Hawthorne, who have combined this chemical evidence with topological theory and steric information to suggest<sup>1</sup> that these  $CH'$  units are axial. The molecular structure tentatively suggested by them has been confirmed for  $B_7C_2H_{11}(CH_3)_2$  as described below. In addition, we have applied a new nonempirical (no experimental parameters) molecular orbital theory<sup>2,3</sup> to  $B_7C_2H_{13}$ , in which the axial hydrogen atoms are shown to be substantially more positively charged than the equatorial hydrogen atoms of the  $CH_2$  groups in the ground electronic state. Since both  $CH$

units of a  $CH_2$  group are terminal, this result may provide a basis for understanding the readily exchangeable axial protons in this molecular species.

### Structure Determination

A needlelike crystal, about 0.2 mm in diameter and 0.7 mm in length, was grown by slow sublimation under vacuum near room temperature and was then sealed into a thin-walled glass capillary tube in a drybox. Weissenberg and precession photographs taken with the long axis ( $c$ ) mounting indicated reciprocal lattice symmetry of  $C_{2h}$ , and Al-powder diffraction calibration established unit cell parameters of  $a = 10.56 \pm 0.02$ ,  $b = 17.35 \pm 0.02$ ,  $c = 5.57 \pm 0.01$  Å, and  $\beta = 82.4 \pm 0.2^\circ$ . Extinctions of  $0k0$  when  $k$  is odd and of  $h0l$  when  $h + l$  is odd indicate the space group  $P2_1/n$ . If four molecules are placed in the unit cell, the reasonable calculated density of  $0.92$   $g\ cm^{-3}$  is obtained.

Relative intensities of 1823 independent reflections were measured on levels  $hkL$  for  $0 \leq L \leq 6$  on the Buerger automated X-ray diffractometer. The  $\omega$  scan

(1) F. N. Tebbe, P. N. Garrett, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **88**, 607 (1966).

(2) M. D. Newton, F. P. Boer, and W. N. Lipscomb, *ibid.*, **88**, 2353 (1966).

(3) F. P. Boer, M. D. Newton, and W. N. Lipscomb, *ibid.*, **88**, 2361 (1966).