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Preliminary communication

A CHLORINE-SUBSTITUTED BORO-ADAMANTANE $(BCl)_6(CH)_4$

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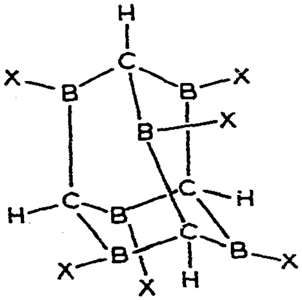
Summary

Thermal degradation of 1,2-bis(dichloroboryl)ethane gives low yields of a white solid $(BCl)_6(CH)_4$ which has a hexaboro-adamantane structure. Substitution of the chlorine atoms by bromine or methyl occurs on treatment with BBr_3 and $Sn(CH_3)_4$, respectively.

The pyrolysis of trimethylboron at 450° has been shown by Brown, Holliday and Way [1] to give a 25% yield of a compound, $(BCH_3)_6(CH)_4$, which has an adamantane-like structure (Ia; X = CH_3):



(Ia) X = CH_3
(Ib) X = Cl
(Ic) X = Br

During studies [2] on the thermal decomposition of 1,2-bis(dichloroboryl)ethane, $Cl_2BCH_2CH_2BCl_2$, at temperatures between 400 and 500° a low yield of an unidentified, white solid was obtained [3], in addition to the many products described in ref. 2. This solid sublimed reproducibly at 66—67° (ca. 0.1 mm Hg) and was very rapidly hydrolysed by water to give chloride ions. We have repeated this work in an effort to identify the solid.

1,2-Bis(dichloroboryl)ethane, made by the reaction of ethylene with diboron tetrachloride at —78°C [4], was placed in an all-glass reaction vessel provided with a constriction and a break-seal. The tube was evacuated, sealed off at the constriction and placed in an oven at 400—500°. After some hours the tube, which showed signs of considerable charring, was removed from the oven, opened up to a vacuum line via the break-seal and all material volatile at room temperatur pumped away. By gently fanning the tube with a free flame the white solid could be sublimed free of the char products in the reaction tube and into the clean apparatus above the break-seal; the compound then was introduced into a mass spectrometer (via a direct insertion probe) using a nitrogen-flushed glove bag sealed onto the entry port of the spectrometer. The complex pattern of peaks making up the parent ion in the mass spectrum (see Fig. 1) indicated the presence of at least several atoms of boron and chlorine; the mass number of the most intense line in the parent ion cluster was 330. Using a published [5] computer program, the theoretical isotopic patterns were calculated for all possible combinations of B, Cl, C and H which would give a cluster of isotopomeric ions at around *m/e* values of 330. The only theoretical pattern which would fit the experimentally observed parent ion was that for the formula $(BCl)_6(CH)_4$; see Fig. 1. The close fit of the calculated and observed line intensities shows that there is virtually no cleavage of single hydrogen atoms from the parent molecule.

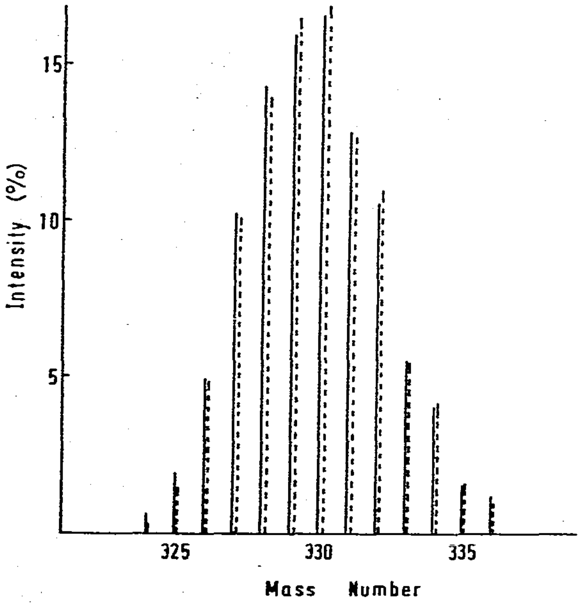


Fig. 1. Comparison of the observed (solid line) and theoretical (broken line) mass spectral intensities for the molecular ion $(BCl)_6(CH)_4^+$.

The only metastable peak we could detect in the mass spectrum of $(BCl)_6(CH)_4$ was an exceedingly strong one centred at about 262 mass units (due to the number of isotopes of the various elements making up the compound this metastable peak was about ten mass units wide):

$$\underset{(330)}{B_6Cl_6C_4H_4^+} \rightarrow HCl + \underset{(294)}{B_6Cl_5C_4H_3^+}$$

The calculated position for the metastable peak, using the *m/e* values for the strongest line in both the parent and daughter ions was 262.0 mass units. This ready cleavage of HCl from the parent ion of $(BCl)_6(CH)_4$ is in direct contrast to the mass spectra of boron-chloride cluster compounds (e.g. B_9Cl_8H and $B_9Cl_7H_2$) which show no cleavage of HCl but have quite intense metastable peaks corresponding to the loss of both $BHCl_2$ and BCl_3 molecules. The formula, the very high thermal stability, the mass spectral behaviour and the extreme sensitivity towards water all led us to the conclusion that the compound had the adamantane-like structure of Ib in which X = Cl.

The exceptional sensitivity of $(BCl)_6(CH)_4$ towards air and moisture made a spectral study of the compound very difficult. A Raman spectrum of the solid sealed in a pyrex tube was the easiest to obtain and this revealed the C—H stretching vibration at a shift of 3000 cm^{-1}; the strong similarity between this Raman spectrum and that of $(BCH_3)_6(CH)_4$, see Fig. 2, proves that the two compounds have a common skeleton. Those absorptions which move to lower Raman shifts on substitution of methyl groups for the heavier chlorine atoms are found at even lower shifts in the hexabromo derivative $(BBr)_6(CH)_4$. A detailed discussion of the infrared and Raman spectra of Ia, Ib and Ic will be given in a later paper [6]. A sample of $(BCl)_6(CH)_4$ dissolved in boron trichloride exhibits a single peak at τ 5.91 (dioxane used as external reference) in the nuclear magnetic resonance spectrum. This is close to the value of τ 6.02 reported for $(BCH_3)_6(CH)_4$, the slight difference being in the correct direction for substitution of methyl groups by more electronegative chlorine atoms.

For $(BCl)_6(CH)_4$ to be formed there must have been some cleavage of the C—C bonds in 1,2-bis(dichloroboryl)ethane; the presence of methane and methyl-

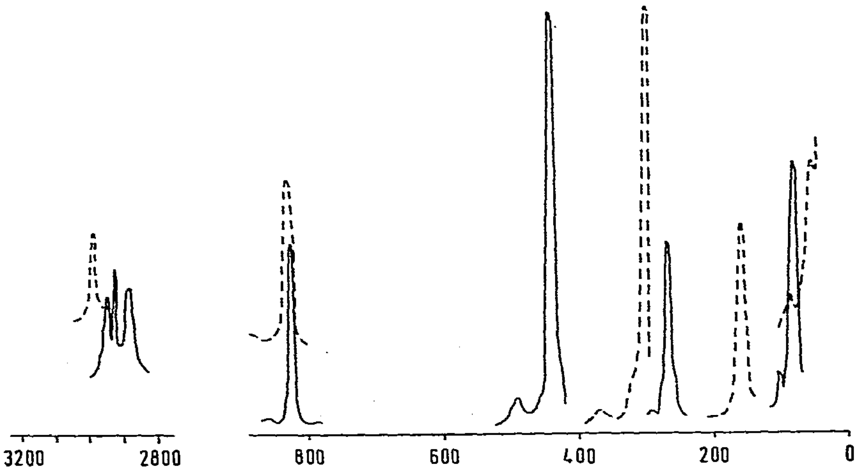


Fig. 2. Principal peaks in the Raman spectra of solid samples of $(BCl)_6(CH)_4$, broken line, and $(BCH_3)_6(CH)_4$, solid line. The sample of the hexamethyl derivative was kindly provided by Dr. M.P. Brown of Liverpool University. The Raman shifts of the more intense peaks are: $(BCl)_6(CH)_4$: 3000, 841, 306, 170, 94, 65 cm^{-1}; $(BCH_3)_6(CH)_4$: 2986, 2951, 2926, 830, 447, 276, 91 cm^{-1}.

boron dichloride among the products previously identified shows that C—C cleavage certainly occurs at some stage during the decomposition. If a better synthesis can be found for this compound, the reactivity of the boron—chlorine bonds should allow the preparation of a whole range of substitution products. For example, we have shown that exchange of halogen occurs with boron tribromide producing $(BBr)_6(CH)_4$ and that treatment with tetramethyltin gives the mixed chloromethyl compounds $B_6(CH_3)_3Cl_3(CH)_4$ and $B_6(CH_3)_4Cl_2(CH)_4$. A trace impurity in the $(BCl)_6(CH)_4$ has a molecular ion in its mass spectrum corresponding to $(BCl)_6(CH)_3CCH_3$ showing that the adamantane skeleton is stable with substituents other than hydrogen on at least one of the carbon atoms. The methyl protons in this compound give rise to a single peak at τ 8.56 in the NMR spectrum; in Ia the methyl groups, which are bonded to boron atoms, give [1] a singlet at τ 9.43.

References

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