SOME THERMODYNAMIC MEASUREMENTS ON ORGANO-BORON COMPOUNDS

A thesis submitted by Geoffrey Brian Watts in candidature for the degree of Doctor of Philosophy of the University of London.

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ABSTRACT

The symmetrical thioboranes $(RS)_3B$, where R= methyl, n-propyl, n-butyl, n-amyl and phenyl, have been synthesized. Standard heats of formation and the energy (E) of the boron-sulphur bond were evaluated for each compound in the series. E(B-S) was found to be nearly constant except for trimethylthioborane.

The synthesis and thermochemistry of tricyclohexylboron and compounds of the series $\varnothing_{3-n}BX_n$ where X= Cl, Br and n= 0,1,2, have been carried out. Standard heats of formation, enthalpies of transition and boron-carbon bond energies of these compounds are reported. the strength of the boron-phenyl bond was found to increase with successive replacement of phenyl by halogen, and this was interpreted in terms of structural features. The results of a single crystal X-ray crystallographic examination of triphenylboron are given.

The synthesis and thermochemistry of the substituted 2-chlorobenzo-2-bora-1,3-dioxarole derivatives are reported. The conjugative effect of substituents in the aromatic ring on the adjacent dioxaboron ring was found to be negligible. Comparison of the experimental heats of formation with those calculated from a standard set of bond energies indicated that these molecules were strained to the extent of 12 Kcal.mole^{-1}. This was interpreted in terms of two opposing effects, (i) strain in the five-membered ring and (ii) resonance energy. A simple geometric method for estimating strain energies in boron heterocycles is derived and discussed.

ACKNOWLEDGEMENTS

The author sincerly thanks Dr. A. Finch for his continual advice and encouragement during the supervision of this work, Drs.P.J. Gardner and E.J. Pearn for much helpful discussion and Professor D. Rodgers of Imperial College for the X-ray crystallographic data.
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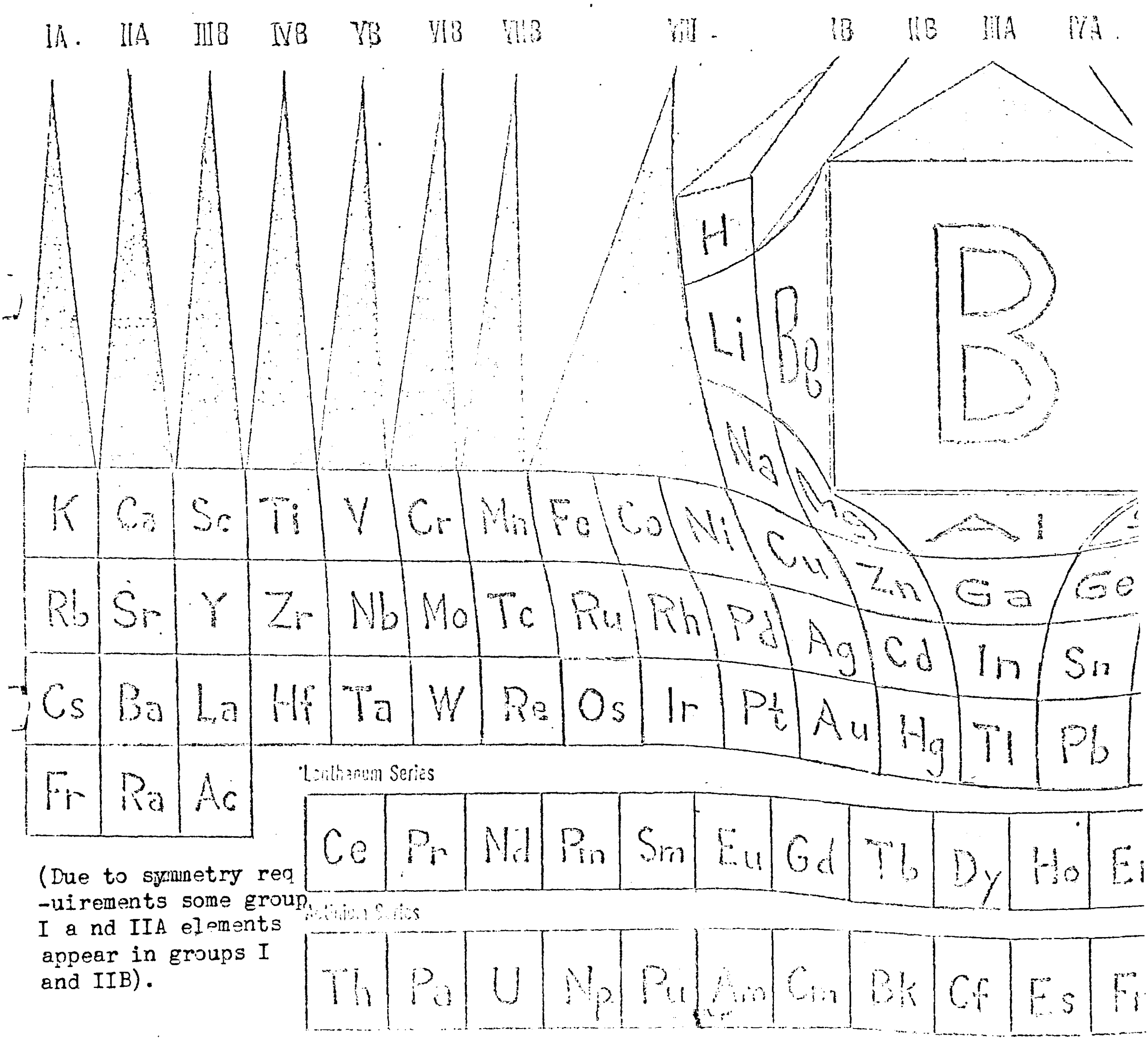
IMPROVED PERIODIC CHART OF BORON AND RELATED EL



(Due to symmetry req-uirements some group I a nd IIA elements appear in groups I and IIB).

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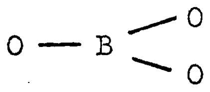
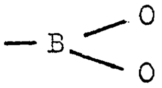
NOMENCLATURE

The nomenclature used to describe boron compounds in this thesis is as follows:-

Compounds containing the nucleus-



are designated borates



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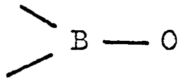
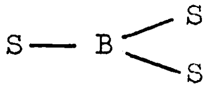
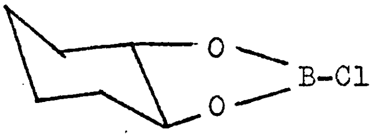


are designated borinates

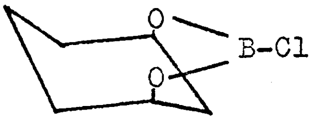


are designated thioboranes

Cyclic boron compounds. Five-membered rings are identified as -olans and six-membered rings as -inans. The bicyclic molecules are termed (arbitrarily)-

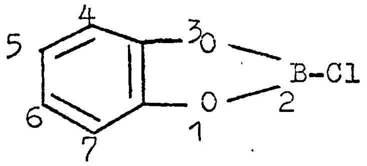


2-chloro-1,3,2-hexahydrobenzo-dioxaborolan (cis or trans)

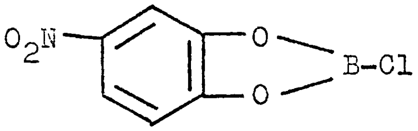


2-chloro-1,3,2-hexahydrobenzo-dioxaborinan.

Dewar's(1) nomenclature is used to describe the heteroaromatic boron compounds-



2-chlorobenzo-2-bora-1,3-dioxarole



2-chloro(5-nitro)benzo-2-bora 1,3-dioxarole

The prefix 'ara' is included to indicate the aromatic nature of these compounds.

INTRODUCTION

The many aspects of organo-boron chemistry have been reviewed comprehensively in the past few years. Steinberg's(2) extensive work 'Organo-Boron Chemistry' covers boron-oxygen and boron-sulphur compounds (Volume I), and boron-nitrogen and boron-phosphorus compounds (Volume II). Boron-nitrogen chemistry has also been the subject of two further publications(3)(4) and Gerrard's book 'The Organic Chemistry of Boron' surveys the whole field in a general way. There have also been several specialist reviews(6)(7).

The thermochemistry and thermodynamic properties of organo-boron compounds have received scant attention. One of the reasons for this is the lack of reliable data for simple boron compounds. The usual method for determining the heat of formation of a compound is to combust it in excess oxygen under pressure in a bomb calorimeter. This technique, however, was not successful with boron compounds because of the difficulty in defining the final thermodynamic state, e.g., most of the boron is oxidised to B_2O_3 which partially hydrates, and in addition there is generally a small amount of residue which contains both B_4C and elemental boron. However, this method has been applied to a few organo-boron compounds, by making corrections for the unburnt material. Fluorine-bomb calorimetry has been used successfully to investigate mainly inorganic-boron compounds.(8) But the technique that has found most application in organo-boron thermochemistry is that of reaction calorimetry. Once the reaction has been established as quantitative, it is thermally monitored at constant pressure and generally at ambient temperature. Hydrolysis, hydroboration, aqueous oxidation and reduction are the types of reactions which have been studied.

Much of the work in the field of organo-boron thermochemistry has been due to Skinner and his collaborators. From 1952 onwards Skinner published a series of papers on this subject. In the initial paper Skinner et al(9) investigated the trialkyl borates $(RO)_3B$, via their hydrolyses since they readily hydrolyse to alcohol and boric acid. The standard heats of formation (ΔH_f^o) of these compounds were derived from the known heat of formation of boric acid and the alcohol. In addition the mean bond dissociation energy ($\bar{D}$) of theboron-oxygen bond was evaluated. $\bar{D}$ is defined as:-

$$\bar{D}\ (B-O) = 1/3\ (D_1 + D_2 + D_3)$$

where D_1, D_2 and D_3 are the individual bond dissociation energies for the processes

$$B(OR)_3 \longrightarrow B(OR)_2 + OR \quad \Delta H_1 = D_1$$

$$B(OR)_2 \longrightarrow B(OR) + OR \quad \Delta H_2 = D_2$$

$$B(OR) \longrightarrow B + OR \quad \Delta H_3 = D_3$$

all components of these equations are in the gas phase.

$$D_1 + D_2 + D_3 = \Delta H_f^o (B,g) + 3\Delta H_f^o (OR,g) - \Delta H_f^o (R_3BO_3,g).$$

The enthalpy of formation of the radical RO,g was determined indirectly from the bond dissociation energies of the alcohols or from the thermal data on the decomposition of alkyl nitrates and nitrites.

$$\Delta H_f^o (OR, g) = D(R-OH) + \Delta H_f^o (ROH,g) - \Delta H_f^o (H,g)$$

for R = Bu^t.

$$RO.NO\ (g) \longrightarrow RO\ (g) + NO\ (g)$$

$$RO.NO_2\ (g) \longrightarrow RO\ (g) + NO_2\ (g)$$

The final estimate of the B-O bond dissociation energy in the trialkylborates was 110 ± 5 $Kcal.mole^{-1}$. This value is based on a value of the heat of sublimation of boron = 97.2 $Kcal.g.-atom^{-1}$ The figure now recommended by JANAF thermochemical tables$^{(10)}$, obtained by a weighted average of many determinations, is 132.8 ± 4.o $Kcal.g.-atom^{-1}$. This increases Skinner's estimate to 122 ± 5 $Kcal.mole^{-1}$. All future values of bond energy or standard heats of formation quoted in this thesis will be based on $\Delta H_f^o (B,g) = 132.8 \pm 4\ Kcal.g.-atom^{-1}$.

Tri-n-butylboron and the di-n-butylboron halides were subsequently studied$^{(11)}$. The reaction found most suitable for calorimetric investigation of tri-n-butylboron, was its reaction with hydrogen halide, a reaction which proceeds at moderate speeds at 60°C.

$$Bu_3^nB + HBr \longrightarrow Bu_2^nBBr + n-C_4H_{10}$$

The extent of the reaction was determined by measuring the volume of n-butane evolved. The above reaction was also used to prepare the di-n-butyl halides (Bu^n_2BX). Only the iodide could not be obtained pure (90 - 95%) since it had a similar volatility to tri-n-butylboron. The halides hydrolyse quantitatively according to the following equation:

$$Bu^n_2BX\ (liq) + (n + 1)H_2O \longrightarrow Bu^n_2BOH\ (liq) + HX.nH_2O$$

The enthalpy of this reaction was measured. Di-n-butylborinic acid is a sparingly soluble oil which undergoes aerial oxidation. Thus these reactions were carried out under a nitrogen atmosphere. The assumption that $D(Bu^n_2B\text{-}Cl)$ is the same as $\bar{D}(B\text{-}Cl)$ in boron trichloride, leads to the following bond dissociation energies:

$D(Bu^n_2B\text{-}OH) = 130$ $\qquad D(Bu^n_2B\text{-}Br) = 87$

$D(Bu^n_2B\text{-}I) = 68$ $\qquad \bar{D}(Bu^n\text{-}B) = 84.5$

all values are in $Kcal.mole^{-1}$.

The mean bond dissociation energy of the boron-nitrogen bond $\bar{D}(B\text{-}N)$ was obtained(12) by studying the hydrolysis of tris-dimethylaminoborane in acid solution.

$$B(NMe_2)_3 + 3H_2O + 3HCl \longrightarrow H_3BO_3 + 3NH_2Me_2Cl$$

Combination of the enthalpy change in this reaction with the standard data, yielded the enthalpy of formation of $B(NMe_2)_3$. This value was combined with a value of $D(H\text{-}NMe_2)$

to give an estimate of $\bar{D}(B\text{-}NMe_2)$. In this paper Skinner also compared the bond dissociation energies of the co-ordinate and covalent links.

e.g., $D(B\text{-}NR_2)$ and $D(BMe_3 \leftarrow NR_2)$
$D(B\text{-}OR)$ and $D(BMe_3 \leftarrow OR)$
where $R = H, Me, Et$.

He found that in general the covalent bond strength was an order of magnitude greater than that of the dative bond.

Diborane is found(13) to add rapidly to olefins at room temperature in the presence of organic ethers to form trialkylboranes in high yields. Skinner et al(14) have exploited this hydroboration reaction thermochemically to determine the heats of formation of trihexyl, heptyl and octylboranes.

$$B_2H_6 + 6(RCH{=}CH_2) \longrightarrow 2B(CH_2CH_2R)_3$$

The reaction was carried out in a specially designed calorimeter, by dissolving the olefin in 'diglyme' or 'monoglyme' solution and then adding a measured volume of diborane. The hydroboration of ethylene, isobutene, butadiene, and isoprene has also been studied(15). Ethylene and isobutene readily give triethylboron and triisobutylboron, but the reaction of diborane with butadiene and isoprene is complicated by a series of competing addition reactions to give complex organoboranes and is not really suited to thermochemical study. A similar technique has been used by Skinner and Bennet(16) in the reaction of diborane with acetone and propan-2-ol, in both cases the reaction is fast and quantitative and yields the same product: di-isopropoxyborane.

$$B_2H_6 + 4(CH_3)_2CO \longrightarrow 2\left[CH_3CH(CH_3)O\right]_2BH......(1)$$

$$B_2H_6 + 4CH_3CH(CH_3)OH \longrightarrow 2\left[CH_3CH(CH_3)O\right]_2BH\ ...(2)$$

The reactions were carried out either by passing diborane into pure second reactant or into a hexane solution of it. Values of the standard heat of formation of di-isopropoxyborane derived from the two reactions are in good agreement with one another.

reaction(1) $\Delta H_f^o\left[(i\text{-}Pro)_2BH,liq.\right] = -184.0 \pm 1.3$ Kcal.mole^{-1}

reaction(2) $\Delta H_f^o\left[(i\text{-}Pro)_2BH,liq.\right] = -183.7 \pm 0.8$ Kcal.mole^{-1}

Finally Skinner(17)(18) has examined the concept of 'redistribution reaction'. A gaseous 'redistribution reaction' is defined as one in which bonds change in relative position but not in total number or formal character.

e.g., $\tfrac{1}{2}MX_2 + \tfrac{1}{2}MY_2 \longrightarrow XMY$

If the assumption of constant transferable mean bond dissociation energies holds then the above reaction should be thermoneutral. Skinner has applied this concept to the series $B(NMe_2)_nCl_{3-n}$ and $B(OEt)_nCl_{3-n}$, by investigation of the heats of hydrolysis of the remaining members of these series, where n = 1,2 and has shown the thermoneutrality assumption to be invalid.

$$\tfrac{1}{3}B(NMe_2)_3\ (g) + \tfrac{2}{3}BCl_3\ (g) \longrightarrow B(NMe_2)Cl_2\ (g) \ \ldots\ldots \quad \Delta H = -12\ Kcal.mole^{-1}$$

$$\tfrac{2}{3}B(NMe_2)_3\ (g) + \tfrac{1}{3}BCl_3\ (g) \longrightarrow B(NMe_2)_2Cl\ (g) \ \ldots\ldots \quad \Delta H = -9\ Kcal.mole^{-1}$$

$B(NMe_2)Cl_2$ (g) and $B(NMe_2)_2Cl$ (g) are more stable by 12 and 9 Kcal.mole^{-1} respectively, than would be the case if the B-Cl bonds should have the same mean bond energy as in boron trichloride and the B-NMe_2 bonds should have the same energy as in trisdimethylaminoborane. A similar trend is also found in the $B(OEt)_n Cl_{3-n}$ series, with $B(OEt)_2Cl$ (g) and $B(OEt)Cl_2$ (g) more stable by 4 and 5 Kcal.mole^{-1} respectively. This additional stabilization was attributed to back co-ordination from the nitrogen and oxygen lone pair electrons to the vacant $2p_z$ orbital of the boron atom. Skinner applied a molecular orbital treatment to these molecules and found that this π stabilization was also derived if it was assumed that the order of effectiveness in back co-ordination to the boron atom is $N > O \gg Cl$. It was noted that this order is reflected in the strengths of the co-ordinate bonds (D) in Lewis acid-base complexes.

TABLE I

Complex	D (Kcal.mole^{-1})
$Me_3N \longrightarrow BF_3$	~ 28
$Et_2O \longrightarrow BF_3$	~12.5
Alkyl chloride/BF_3	No complex is generally formed

However, this relationship is possibly fortuitous in view of the factors which can affect the strength of a donor-acceptor bond and which are not relevant to back co-ordination. To attribute the heats of redistribution entirely to back co-ordination may be an over-simplification and it may be that steric effects (between the bulky NMe_2 groups) are important. Back donation from oxygen to boron in alkylborates is also indicated by the low acceptor power of these compounds. Although trimethylborate will form co-ordination compounds with ammonia and amines, the other alkylborates do not. The fact that triphenylborate forms stable complexes with ethylamine and pyridine, is attributed to the mesomeric interaction between the oxygen lone pairs and the π electrons of the aromatic ring.

Skinner's studies on the strength of the B-O bond in alkylborates and the general lack* of thermodynamic information on boron-sulphur compounds has promted an investigation into the boron-sulphur bond energy in alkylthioboranes $(RS)_3B$. The investigation forms the first part of this thesis. *The only thermodynamic datum recorded(19) is a mass spectroscopic study of the volatile species above ZnS(cryst) and B(cryst) at 700-900°C which indicated the presence of B_2S_3. A very approximate figure for the enthalpy of formation in the gas phase (-11 ± 10 $Kcal.mole^{-1}$ was quoted and the boron-sulphur bond energy was calculated to be 100 ± 14 $Kcal.mole^{-1}$.

Stone(20) has summarized the available thermochemical data for boron trihalide addition compounds and this suggests that the order of relative acceptor power is $BBr_3 > BCl_3 > BF_3$, which is the reverse of that expected from electronegativity and steric considerations. This sequence of acceptor strength was ~~confirmed~~ first indicated by Brown and Holmes$^{(21)}$ who measured the heats of reaction of pyridine with the three boron halides in nitrobenzene solution.

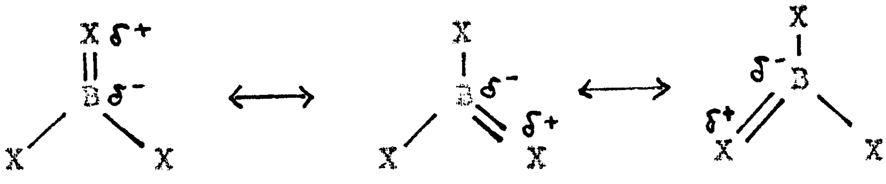
$$BX_3 \text{ (nitrobenzene solution)} + C_5H_5N \text{ (nitrobenzene solution)}$$
$$= C_5H_5N{:}\ BX_3 \text{ (nitrobenzene solution}$$

The results are tabulated:

TABLE II

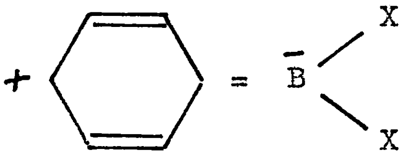
Halide	Heat of Reaction K cal.mole^{-1}
BF_3	25.0 ± 1.0
BCl_3	30.8 ± 0.2
BBr_3	32.0 ± 0.2

Although these values do not refer to the gas phase reactions, it is unlikely that the order of acceptor strength would be altered by correction to the gas phase. An explanation can be advanced in terms of $P\pi - P\pi$ bonding between boron and the halogens, the extent depending on the halogen.



It is probable that similar $P\pi - P\pi$ bonding occurs in substituted boron halides, e.g. the aryl boron halides. The literature on this type of compound is rather conflicting.

Some evidence suggests that although $P\pi - P\pi$ bonding between boron and halogen occurs, the main contribution of electron density to the electrophilic boron atom comes from $P\pi - P\pi$ bonding in the phenyl boron bond. Structures of the type, i.e.



have been suggested. Qualitative evidence for carbon-boron π bonding comes from electron diffraction data by Coffin and Bauer.(22 They found the phenyl boron dichloride molecule to be planar and the B - Cl bond length to be the same as that in boron trichloride. Dipole moment measurements(23) on phenyl boron dichloride indicate that resonant structures of the above type contribute to the overall structure of the molecule. Spectroscopic investigations of aryl boron halides have been undertaken by Bellamy(24) et al and Lockhart.(25) Lockhart calculated the barrier to rotation about the boron-carbon link as $\sim$ 45 K cal. mole^{-1} probably indicating considerable π character in the bond. Bellamy found that whereas the infrared spectra of a number of boron monoaryl compounds showed a sharp bond at 1440 - 1430 cm^{-1} (attributed to the B-C$_{aryl}$ stretching), the band in the diphenyl boron compounds had moved to lower frequencies (between 1220 & 1198 cm^{-1}) On the other hand the B-Cl stretch showed little variation in absorption frequency in going from phenyl boron dichloride to diphenylboron chloride. It would be expected if there was an appreciable amount of double bond character in the B-Cl bond, any change in the groups attached to boron would markedly affect the frequency at which the B^{11}-Cl symmetric stretch occurred. Stone et al(26) have reviewed the evidence both chemical and spectroscopic for the bonding in alkyl and arylboron compounds and conclude that carbon-boron π bonding is significant particularly in the substituted boron dichlorides.

However, some evidence leads to the opposite conclusions. Abel et al(27) have investigated the factors influencing the co-ordination of amines to boron attached to oxygen. The results for the complexing of the esters $\phi B(OR)_2$ and ϕ_2BOR with pyridine are summarised.

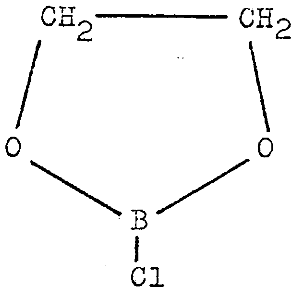
TABLE III

R(in ester)	$\phi B(OR)_2:C_5H_5N$	$\phi_2BOR:C_5H_5N$
Me	stable	stable
Et	unstable	stable
Pr^n	-	stable
Bu^n	-	association

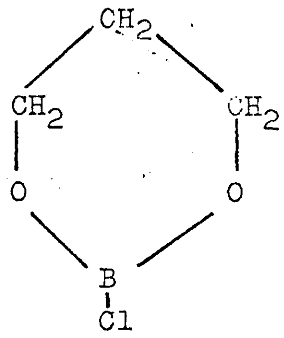
When there was no precipitate, heat of mixing indicated association, whereas a precipitated complex was described as stable if it remained at 20°/20mm. and unstable if under these conditions dissociation occurred. It has already been mentioned that trialkylborates generally give no co-ordination compounds with nitrogen donors. This is attributed to back donation from three atoms of oxygen to nucleophilic boron thus decreasing its acceptor properties. A phenyl group attached to boron, in some way compensates back co-ordination from two oxygen atoms, and substitution of a second phenyl group considerably increases the stability of these complexes. The results indicate that $p\pi - p\pi$ bonding between phenyl and boron is unlikely. Armstrong and Perkins(28)(29) have applied a self-consistant molecular orbital technique to calculate the π electronic structures of phenyl and diphenylboron halides. The conclusions reached in both cases is that electron density on the boron atom originates from the halogen π orbitals and that contributed by the phenyl ring(s) is not significant. Finally in a recent paper, Dewar(30) notes that in a recent study of the ^{11}B nuclear magnetic resonance of several arylboron compounds the resonances for the arylboronic acids appear downfield by ~ 10 ppm, relative to boric acid. This implies that replacement of hydroxyl by phenyl has a deshielding effect on the boron atom. Other workers(31) have also drawn attention to this surprising effect and pointed out that it cannot be attributed to any effect of ring current or unsaturation, for the ^{11}B chemical shifts of phenyl and n-butylboronic acid differ by less than 1 ppm.

In view of these apparent contradictions a thermochemical investigation of the boron-phenyl bond energy in the arylboron halides was undertaken, and the results of this work appear in Section 2,Results and Discussion.

The strain in five and six-membered boron heterocycles has recently been studied thermochemically(32)(33). That the strain is greater in the dioxaborolan than in the dioxaborinan system, is shown by simple stereochemical arguments and also a great deal of chemical evidence.

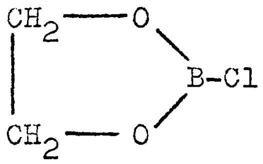


2-chloro-1,3-dioxaborolan



2-chloro-1,3-dioxaborinan

Thus the olan derivatives were found to be associated in solution(34)(35) to a much greater extent than the corresponding inan derivatives. Five-membered boron heterocycles also hydrolyse more readily(36) and form addition compounds with nitrogen donors more easily(37)(38). The driving force in these reactions is attributed to the relief of strain in the borolan system by formation of a tetrahedral configuration around the boron atom. Whereas an sp^2 or sp^3 boron atom may be incorporated into a six-membered ring equally well. In the first paper, the following dioxaboron systems were studied:



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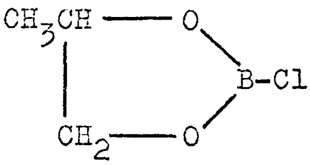

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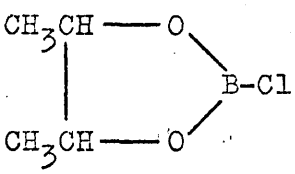

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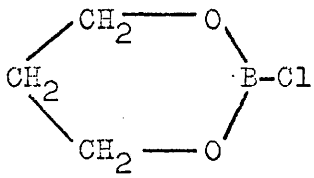
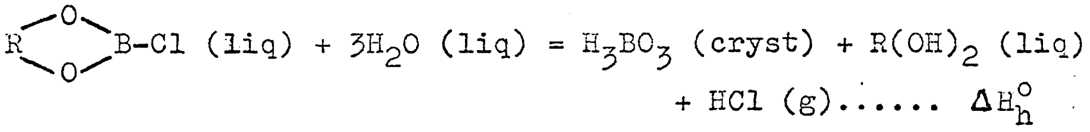


IV

by hydrolysis in a solution calorimeter.



$$R(O)_2B\text{-}Cl\ (liq) + 3H_2O\ (liq) = H_3BO_3\ (cryst) + R(OH)_2\ (liq) + HCl\ (g) \ldots\ldots\ \Delta H_h^o$$

The ring strain, (ΔH_b), in these molecules was defined as the difference in the standard heat of hydrolysis of the compound and that of an unstrained reference compound (diethylchloroboronate).

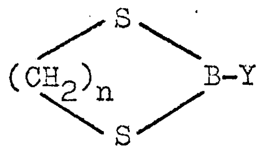
$$\Delta H_b = \Delta H_h^o(RO_2BCl,liq) - \Delta H_h^o(EtO)_2BCl,liq$$

This function was then correlated to the pure phase association (α) in the heterocycles.

TABLE IV

Compound	ΔH_b (Kcal.mole^{-1})	α (Pure phase)
$\overline{OCH_2CH_2CH_2OB}$-Cl	1.4	1.1
$\overline{OCH_2CH_2OB}$-Cl	0.9	5
$\overline{OCHMeCH_2OB}$-Cl	1.2	3
$\overline{OCHMeCHMeOB}$-Cl	2.2	1.1

It will be noted that the greater the substitution (of methyl) in the olan ring, the smaller the association. This is probably caused by the increased steric hinderance to 'stacking structures' which were postulated$^{(35)}$ as a mode of association in the borolans. The value of ΔH_b for compound III (very little association) was considered to be the approximate strain in the dioxaborolan system. Compared with the value of the dioxaborinan(IV) derivative, the difference is surprisingly small. This method, however, gives only a relative measure of the residual strain in the associated species. In the second paper$^{(33)}$ all the components were referred to the gaseous phase rather than to the condensed states. The strain thus obtained, refers to the discrete molecule. In this paper the strain in the thioboron heterocycles was also investigated.



n = 2,3

Y = Cl or Ø

These compounds were hydrolysed in a similar manner to the dioxaboron analogues, but in this case the products obtained depend upon the nature of Y. When Y = Ø, the hydrolysis product is phenylboronic acid. (The standard enthalpy of formation of this 'key' organo-boron compound has been reported(39).)

$\overline{SRSB}\text{-Cl} + 3H_2O \longrightarrow R(SH)_2 + H_3BO_3 + HCl$

$\overline{SRSB}\text{-Ø} + 2H_2O \longrightarrow R(SH)_2 + ØB(OH)_2$

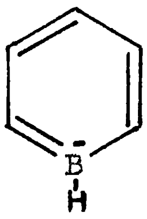
The results obtained are tabulated.

TABLE V

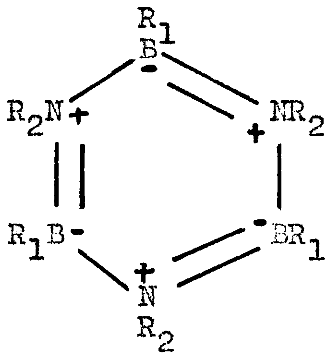
Compound	Degree of association (α') at 0.05M in benzene	Strain energy Kcal.mole^{-1}
$\overline{SCH_2CH_2SB}\text{-Cl}$	1.02	2.8 ± 4.3
$\overline{SCH_2CH_2CH_2SB}\text{-Cl}$	1.08	3.2 ± 4.3
$\overline{SCH_2CH_2SB}\text{-Ø}$	0.99	5.6 ± 4.7
$\overline{SCH_2CH_2CH_2SB}\text{-Ø}$	1.01	5.5 ± 4.7
$\overline{OCH_2CH_2OB}\text{-Cl}$	1.22	highly strained
$\overline{OCH_2CH_2CH_2OB}\text{-Cl}$	1.08	12.7 ± 5.2

The five and six-membered sulphur heterocycles possess approximately equal strain and this is less than in either of the oxygen heterocycles. The smaller strain energy was attributed to the larger boron-sulphur and carbon-sulphur bond lengths which allow an sp^2 boron atom to be contained in a five-membered ring with little strain. Unfortunately the quantitative estimation of the 1:3 dioxborolan ring strain was not possible because the compound boiled over an extensive temperature range, thus precluding the accurate determination of the latent heat of vaporization. However, the pure phase degree of association (α) indicates that it is highly strained.

When, however, a dioxaborolan ring is attached to a conjugated ring system, the possibility of aromaticity in the dioxaboron ring arises. According to the Hückel rule, if a cyclic compound is to be aromatic, each ring atom in it must have a P-orbital available to take part in a conjugated system, and the total number of π electrons for a monocyclic system must be $(4n + 2)$, where n is an integer. Since the carbon atom possesses one more electron than boron, the B^- ion will be isolectronic with neutral carbon. Replacement of carbon in an aromatic system by B^- will therefore give an isolectronic aromatic system.



V.



VI.

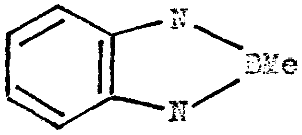
Compound V has not yet been reported, but borazine or borazole (VI $R_1 = H, R_2 = H$) is well known and its properties are strongly indicative of aromatic character. Borazole type molecules have been subject to several thermochemical studies,(40)(41)(42) using both solution and combustion calorimetry. The data for borazole by these two different techniques are in serious disagreement, but the measured heats of formation of B trichloroborazole (R_1 = Cl, R_2 = H) are consistent. The experimental heats of formation of these compounds (standard state and gas phase) are tabulated.

TABLE VI

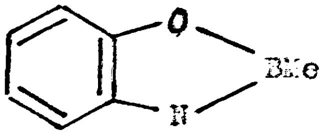
Re.	R_1	R_2	ΔH_f^o (std.state)	ΔH_f^o(g)
40	H	H	-204.9	-197.0
42	H	H	-129.6	-122.6
40	Cl	H	-256.1	-239.2
41	Cl	H	-255.4	-238.2

All values are in K.cal.mole^{-1}

Ulmschneider and Goubean(43) prepared the first known aromatic organo-boron compounds 2-methylbenzo-2-bora-1, 3 diazarole (VII) and 2-methlbenzo-2-bora-3-aza-1-oxarole (VIII) by heating trimethyl boron with O-phenylenediamine and O-aminophenol respectively.

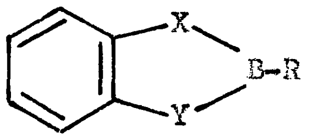


VII



VIII

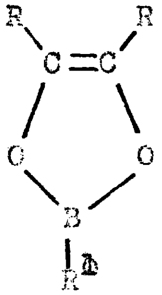
They failed, however, to realise the theoretical interest of these systems. Soon afterwards, a whole series of similar compounds were reported by various workers.(44)(45)(46)(47)



X, Y = O, N, S.

R = ∅, alkyl, Cl, H.

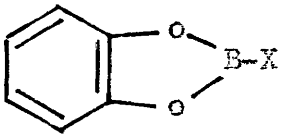
Several monocyclic systems have also been described(48)(49)



R = ∅, CH_3

R^1 = ∅, $(CH_3)_2CH$.

The physical properties of the benzo-2-bora-dioxarole derivatives (VIV) have been most

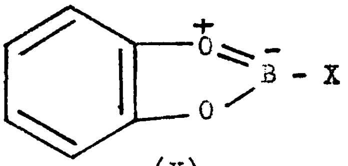


VIV.

widely studied and may be considered typical of this type of molecule.

<u>Spectral properties</u>. Ultraviolet spectra of these compounds showed close similarity, but were quite different from the spectra of the parent ring compound, indicating the presence of analogous conjugated systems.(44) Blau

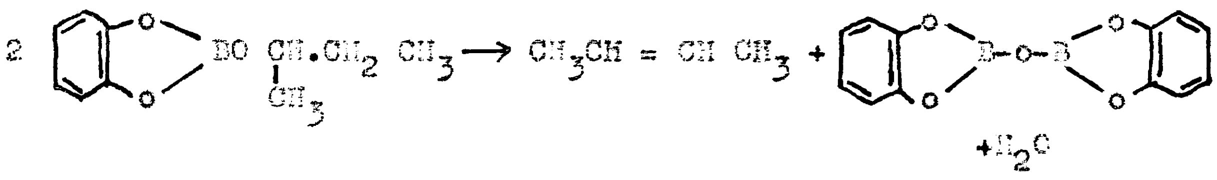
et al(50) have examined the infra-red spectra of a number of 2-substituted benzo-2-bora-1, 3 dioxaroles. The value 1447 ± 40 cm^{-1} was assigned to the ring B-O stretching vibration, a value which is significantly higher than that (1350 - 1310 cm^{-1}) usually found in tervalent boron-oxygen compounds. This implies that the B-O bond order in these compounds is higher than in the trialkyl borates and hence that canonical forms of the type (X) contribute to the structure



(X)

The chloro derivative (X = Cl) showed no absorption band normally associated with the B-Cl bond, which could be due to the lower B-Cl bond order arising from the above canonical structure.

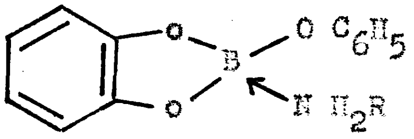
Thermal stability. The benzo-dioxaroles generally show high thermal stability compared with the corresponding acyclic compounds $(RO)_2BX$. The chloroboronate (X = Cl) required prolonged heating at 220 - 230°C in order to demonstrate a clear redistribution into BCl_3 and the bis borate and the bromo derivative (X = Br) showed similar stability. However, the stability of the O-alkyl derivatives was found to be a function of the alkyl group present.(51) The methyl derivative quantitatively disproportionates to trimethyl borate and tricatechol biborate on heating to 240° for 16 hours, and the sec. butyl ester is almost completely decomposed by the reaction.



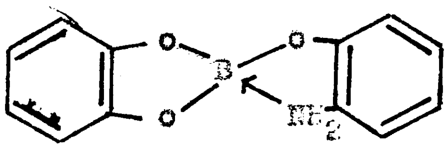
In contrast the n-butyl and n-octyl esters were recovered in 96 and 92% yield respectively on heating for prolonged periods at 300°C. This stability was attributed(51) in part to the aromaticity of the benzo-2-bora-1, 3 dioxarole ring which possesses (4n + 2)π electrons.

Hydrolytic stability. Compared with the analogous non-aromatic boron compounds, their stability towards hydrolysis is high, but it is low compared with the normal aromatic compounds.

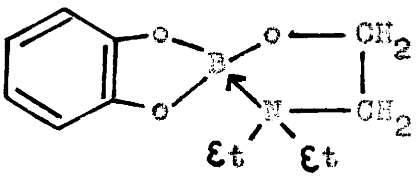
Addition Compounds. In contrast to the symmetrical alkyl borates which do not as a rule form complexes with amines, and like the aryl borates which do complex with amines, alkyl and phenyl esters of benzo-2-bora-1, 3 dioxarole form stable 1 : 1 complexes with pyridine(51) and aniline.(52)



The amino derivatives (XI) and (XII), however, did not give adducts with pyridine or aniline and this was attributed(52) to internal N → B bonding.

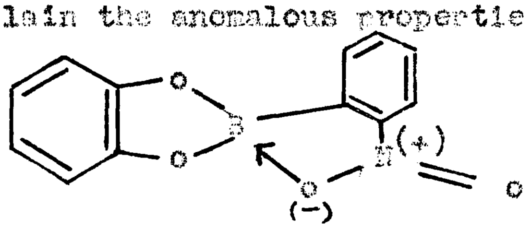


XI.



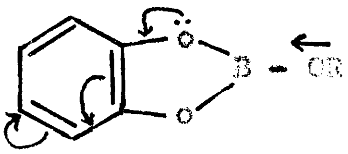
XII.

Hemming and Johnson(47) have also postulated intra-molecular bonding between boron and the ortho nitro group, to explain the anomalous properties of compound XIII.



XIII

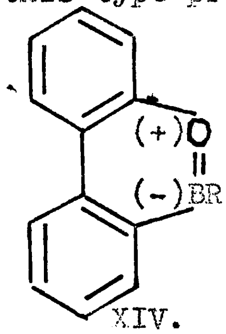
Steinberg(53) considered that in the O-alkyl derivatives the withdrawal of electrons by the -T effect was contrasted to the inductive (+I) effect of the alkyl group and resulted in the boron atom becoming sufficiently electrophilic to promote complexing with amines.



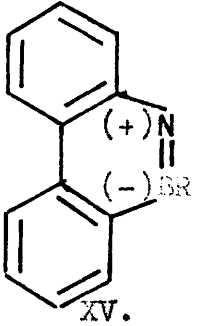
Evidence(54) for this electron shift away from the boron atom was obtained from the solubility relationships of hydrogen chloride in tri-n-butyl borate (0.489 moles HCl per mole of ester at 0°C) compared with 2-butylbenzo-2-bora-1, 3 dioxarole (0.242 moles HCl per mole of ester at 0°C). The solubility of hydrogen chloride is directly related to the electron density on the oxygen atom.

The direction of electron shifts postulated for resonance stabilisation and adduct formation in the benzodioxarole system are directly opposed to one another and consequently the electron shifts are incompatible. It is the object in the final part of this thesis to investigate thermochemically resonance stabilisation in this system and the effect of ring substituents on the stabilisation.

Finally, compounds containing boron in a six-membered aromatic ring were shown to possess exceptional stability. The 10, 9 borazarophenanthrene (XV) and 10, 9 boroxarophenanthrene derivatives (XIV) were the first compounds of this type prepared (by Dewar et al.$^{(55)(56)}$)



XIV.



XV.

R = Cl, oH, C_6H_5, alkyl.

That this stability is due to resonance stabilisation is indicated by (1) the ultraviolet spectra of compounds XVand XIVwhich are very similar to that of phenanthrene and quite different from the parent compound (the substituted Bi-phenyl 2) salt formation by these compounds in alkali involves loss of a proton from the hydroxyl group, whereas boric acid derivatives normally form salts by addition of base to the boron atom. In the former case, however, such an addition would be unfavourable because conversion of the boron atom from sp^2 to sp^3 geometry would remove the aromaticity of the central ring. 10, 9 Borazarophenanthrene compounds are resistant to hydrolysis, even to boiling concentrated hydrochloric acid and concentrated alkali, (cf. the five-membered boron heteroaromatics), and they undergo typical aromatic reactions, i.e. nitration and Friedel Crafts acetylation.

Bond Energy Terms

It would be convenient at this point to consider the definition of bond energy and the application of bond energies to thermochemistry.

The heat of atomisation (ΔH_a^o) of a compound AB_n containing only A - B bonds refers to the process.

$$AB_n(g) \longrightarrow A(g) + n\,B(g)$$

The compound is in the ideal gas state at 25°C and the gaseous atoms are in their electronic ground states also at 25°C. The sum of the bond energies is set equal to the heat of atomisation; thus the bond energy of the A - B bond, E(A-B) is defined by the expression

$$E(A-B) = \frac{1}{n} \Delta H_a^o (AB_n, g)$$

Consider the following thermochemical cycle.

$$\begin{tikzcd}
AB_n, g \arrow[rr, "\Delta H_a^o"] & & A, g + nB, g \\
& \text{elements } A + nB \text{ (standard states)} \arrow[ul, "\Delta H_f^o(AB_n, g)"'] \arrow[ur, "\Sigma\Delta H_f^o \text{ (atoms)}"'] &
\end{tikzcd}$$

~~elements A + nB (standard states)~~

then $\Delta H_a^o = \Sigma \Delta H_f^o(\text{atoms}) - \Delta H_f^o\ (AB_n, g)$

Since reliable values are available for the heats of formation of the gaseous atoms (ΔH_f^o, atoms) of most of the common elements, only the standard heat of formation of the compound, in the gaseous state, need be evaluated in order to determine the bond energy.

Consideration of a molecule with two or more different types of bonds, e.g. CH_2Cl_2, a further assumption is required, For any one molecule the heat of atomisation provides only one datum and can give only the sum of the bond energies of the different bonds. Thus the assumption made was that each bond of a given type has a constant characteristic energy transferable from one molecule to another, and that bond energy terms were additive. Careful experimental work has shown this simple assumption to be invalid and as a result a number of more sophisticated (although empirical) bond energy schemes have evolved. The bond energy schemes which have been utilised in this thesis are now summarised.

1. Laidler(53) considered that although C - C bond energies (E(C-C)) in the paraffin hydrocarbons are constant, the bond energies of the primary ($E_{CH}(p)$), secondary ($E_{CH}(s)$) and tertiary ($E_{CH}(t)$) carbon-hydrogen bonds are not identical.

(There is some experimental work by Lide(59) to support this view). The heat of atomisation (ΔH_a^o) of the paraffin hydrocarbon is given by

$$\Delta H_a^o(C_nH_{2n+2}) = (n - 1)E_{cc}\ (\text{paraffins}) + N_pE_{CH}(P) + N_sE_{CH}(S) + N_tE_{CH}(t)$$

where N_p, N_s and N_t are the numbers of primary, secondary and tertiary C - H bonds in the molecule. The scheme has recently been updated and extended by Mackle et al.(60) Allen(61) has shown that the introduction of a single parameter, i.e. the interactions between next nearest neighbours, removes practically all the deviation from constancy. This parameter is the interaction energy of a pair of carbon atoms which are next nearest neighbours (1 : 3 interaction). A more refined equation for calculation of the heats of atomisation (ΔH_a^o) for a compound R_nX is also derived. This equation takes into account all the steric interactions which can arise in a molecule of the type R_nX.

$$\Delta H_a^o = nB_{cx} + n_1 B_{CH} + n_2B_{cc} + a_1\Gamma + a_2\Delta + a_3\Gamma_{ccx} + a_4\Delta_{ccx} + a_5\Gamma_{cxc} + a_6\Delta_{ccc} \quad - (8)$$

where n and n_2 are the numbers of C - H and C - C bonds; a_1 is the number of C - C - C interactions, a_3 the number of C - C - X interactions and a_5 the number of C - X - C interactions. a_2 is the number of C_3 trios attached to carbon and a_4 the number of C_2X trios attached to carbon; a_6 is the number of C_3 trios attached to X and (S) the total steric repulsion correction. B_{cx} etc. are the effective bond energy terms, and Γ and Δ are constants depending upon the type of interaction.

Cox Scheme(62) This is an extension of an empirical scheme devised by Mackle and O'Hare(59) for aromatic compounds, in which the resonance energy is absorbed into empirical term values Car - Car of the bonds composing the ring.

The Cox and Laidler-Mackle schemes are easiest to apply because of the relatively smaller number of parameters involved. An excellent review of available bond energy schemes is given by Skinner and Pilcher.(63)

Resonance and Conjugation Energies

The usual method of calculating the resonance energy of a molecule is to take a standard set of bond energies from which the heat of formation of one of the resonance structures can be calculated, and compare it with the experimentally determined figure. The magnitude of the resonance energy depends entirely on the reference adopted. Because the resonance energies calculated by this method are made up of contributions of which π conjugation energy is one but not necessarily the major component, Dewar(63) recommends that the energy associated with the delocalisation of π electrons be described as resonance energy, and the term conjugation energy refer to the energy obtained by comparison of experimental and calculated enthalpies of formation. It is conjugation energies which are considered in this thesis.

Strain Energies

Strain energies may be generally divided into three different types: (1) angular strain due to compression of the valency angle, (2) interaction strain due to repulsion betweennon-bonded atoms, (3) torsional strain of double bonds out of plane where the greatest $P\pi - P\pi$ overlap can occur.

By considering an additional term (P) in the bond energy equation, strain and conjugation

$$\begin{tikzcd}
\text{compound,g} \arrow[rr, "\Sigma E"] & & \text{elements,g} \\
& \text{elements (std. states)} \arrow[ul, "\Delta H_f^o{,}g"] \arrow[ur, "\Sigma\Delta H_f^o\ (\text{atoms})"'] &
\end{tikzcd}$$

energies may be derived.

$$\Sigma E - P = -\Delta H_f^o\ (\text{compound, g}) + \Sigma\,\Delta H_f^o\ (\text{atoms})$$

If P is positive it may be interpreted as strain energy and if negative as conjugation energy.

Thermodynamic Conventions

The calorimetry described in this thesis was carried out at constant pressure (atmospheric) and the measured heat of reaction is equal to the enthalpy change (ΔH). Normal thermodynamic conventions are followed in selection of standard states for reactants; the standard state being the most stable form existing at one atmospheric pressure and 25°C. The heat of formation of a substance in this state is denoted ΔH_f^o. The heats of formation of the elements in their standard states are zero. When the reaction is exothermic the enthalpy change is regarded as negative. All heat quantities are quoted in terms of the thermochemical calorie which is defined by the relationship 1 cal. = 4.1840 abs. Joules.

Consider the following hypothetical hydrolysis reaction:

$$(RX)_3B + 3H_2O \longrightarrow H_3BO_3 + 3RXH$$

The observed heat of hydrolysis (ΔH_{obs}) refers to the reaction

$$(RX)_3B\ (\text{std.state}) + (n + 3)H_2O(\text{liq}) = (H_3BO_3 + 3RXH)\cdot nH_2O$$

and the standard heat of hydrolysis (ΔH_h^o) refers to the process

$$(RX)_3B\ (\text{std.state}) + 3H_2O(\text{liq}) = H_3BO_3(\text{cryst}) + 3RXH(\text{std. state})$$

the two functions are connected by the equation

$$\Delta H_h^o = \Delta H_{obs} - \Delta H_s\ (\text{reaction products})$$

ΔH_s = heat of solution at 25°, with a final thermodynamic state $H_3BO_3.nH_2O$ or $RXH.\frac{n}{3}H_2O$. ΔH_s^o is the heat of solution at 25° and at infinite dilution ($N = \infty$). The difference between this and ΔH_s at concentration N is the heat of dilution. Heats of dilution are very small and generally less than the limits of accuracy obtainable with the calorimeter, and consequently heats of dilution are neglected (but not in cases where hydrogen chloride gas is the product). Heats of mixing are also neglected.

Treatment of Errors

It is customary(57) in combustion calorimetric work, to quote errors as twice the standard deviation from the mean, even with only three observations. In this thesis the following procedure with regard to errors is adopted.

(1) For less than five observations the error is taken as the range.

(2) For five or more observations the error is quoted as twice the standard deviation from a single observation.

The net error is calculated as the root of the sum of the squares of the constituent errors.

RESULTS AND DISCUSSION

Section I. The Thermochemistry of the Trialkylthioboranes and Triphenylthioborane

Purpose of Investigation

To synthesize the symmetrical thioboranes $(RS)_3B$, where R = Me, n - Pr, n - Bu, n - Am and Ph, and determine the value of the boron-sulphur bond energy in the series. (Triethylthioborane has already been studied in this laboratory)(33)

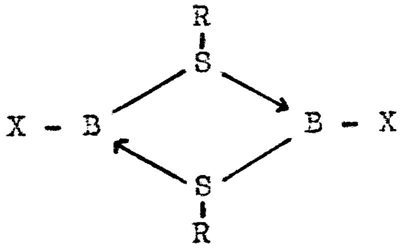
Methods of Preparation

Alkyl and arylthioboranes are generally prepared by two main methods.

(1) Condensation of alkane thiol (3 moles) with boron trihalide (1 mole) in a suitable solvent, e.g. benzene or methylene chloride.

$$3RSH + BX_3 \longrightarrow (RS)_3B + 3HCl$$

The yield of thioborane obtained by this direct method is, in some cases, poor because of the formation of the dimeric species(65) XVI.



XVI.

The problems of incomplete reaction are overcome in the second method which makes use of metal mercaptides. (2) Reaction of lead, silver or sodium mercaptides with boron tribromide in benzene yields the corresponding trialkyl or arylthioborane(65)

$3AgSR + BBr_3 \longrightarrow (RS)_3B + 3AgBr.$

Many other general methods of synthesis are available and these have been summarised by Lappert.(66)

Triphenylthiobrane was prepared according to the procedure of Young and Anderson(67) by refluxing thiophenol (3 moles) with boron trichloride (1 mole) in benzene solution. These workers attempted to purify the phenylthioborane by recrystallisation from benzene, but found that the melting point was not sharp (129 - 143°), even after several recrystallisations. In this preparation the compound was purified by distillation at reduced pressure and a pale yellow solid was obtained which had a sharper melting point (140 - 143°). All the alkylthioboranes used in this work were conveniently prepared by the method of Mikhailov and Bubnov.(68) Alkanethiol was added to boron trichloride in ether solution at -80°C to give a 1 : 1 complex. On warming the reaction mixture to ambient temperature, hydrogen chloride gas was liberated and was abstracted with triethylamine. After filtration of triethylamine hydrochloride and removal of the solvent, the alkylthioboranes were purified by vacuum distillation. All the trialkylthioboranes were colourless, mobile liquids. The preparation, analysis and handling of these compounds are described in detail in the experimental section.

Trialkyl and triphenylthioboranes are readily hydrolysed according to

$(RS)_3B + 3H_2O \longrightarrow H_3BO_3 + 3RSH.$

The thiols produced are slightly water soluble and therefore all hydrolyses were performed in saturated solutions of the thiols; in this way the thiols produced by hydrolysis can be assumed to be in their standard states. The reaction was also carried out under a nitrogen atmosphere since both thioboranes and the thiols are susceptible to aerial oxidation.

For trimethylthioborane, the product (methanethiol) was gaseous. Any thermal effect due to evolution of gas, e.g. direct thermal transfer or from vapourisation of water was assumed negligible in comparison with the heat quantities being measured.

ΔH_{obs}, the measured heat of reaction, refers to the process

$(RS)_3B$ (liq or cryst) + $(n + 3)H_2O$(liq) $=$ $3RSH$(liq. or g)
+ $H_3BO_3.nH_2O$

from which

ΔH_f^o ((RS)$_3$B, liq or cryst) = ΔH_f^o($H_3BO_3.nH_2O$) + 3ΔH_f^o (RSH, liq or g) - 3ΔH_f^o(H_2O) - ΔH_{obs}.

Ancillary thermodynamic data used to calculate the standard heats of formation of the thioboranes is collected in Table VII.

TABLE VII

Species	ΔH_f^o:298 (K.cal.mole^{-1})	Source
H_2O liq.	-68.32	69
H_3BO_3, aq.	-256.5 ± 0.2	72
CH_3SH, g.	-5.46 ± 0.2	70
C_2H_5SH, liq.	-17.62 ± 0.11	70
n - C_3H_7SH, liq.	-29.76 ± 0.16	70
n - C_4H_9SH, liq.	-29.76 ± 0.28	70
n - $C_5H_{11}SH$, liq.	-36.11 ± 0.40	70
C_6H_5SH, liq.	+15.02 ± 0.27	70

The heats of formation of the alkanethiols have recently been revised(71) using more modern thermodynamic data, but the values have not changed significantly.

The determination of the bond energies in these compounds, require that the standard enthalpy of formation of the compound in the gaseous state be known. Hence the latent heats of vapourisation of the symmetrical thioboranes were determined. The method used was a dynamic distillation technique, establishing an equilibrium between liquid and vapour and stabilising the pressure with a cartesian monostat (see Experimental section 4).

The experimental data are represented in the form

$$\log_{10}P_{(mm)} = a - \frac{b}{T^{o}K}$$

where a and b are constants. Values of a and b were calculated from a least squares analysis and they are collected, together with the latent heats of vapourisation ($\Delta H^{T}vap$), for the trialkyl thioboranes, in Table VIII.

TABLE VIII

Compound	Range $T^{o}C$	a	$10^{-3}b$	$\Delta H^{T}vap.$ K.cal.Mole	$\Delta H^{298}vap.$ $K.cal.mole^{-1}$
$(CH_3S)_3B$	30-120	8.964	2.965	12.3	12.9 ± 0.2 (74)
$(C_2H_5S)_3B$	-	-	-	-	14.6 ± 0.5 (33)
$(n\text{-}C_3H_7S)_3B$	150-210	10.32	3.98	18.2	20.8 ± 0.5
$(n\text{-}C_4H_9S)_3B$	167-230	10.55	4.38	20.0	22.9 ± 0.5
$(n\text{-}C_5H_{11}S)_3B$	173-230	10.86	4.82	22.05	25.0 ± 0.5
$(C_6H_5S)_3B$	-	-	-	-	26.0 ± 1.5

Values of $\Delta H^{T}vap$ refer to the mean value of the temperature range over which the experimental measurements were taken. Application of Watson's (73) equation (see Experimental section 4) reduces this datum to 298°K.

The boiling point of triphenylthioborane was too high to permit determination of its latent heat of vapourisation by this method. It was estimated from a graph of molecular weight against ΔH_{vap}^{298} of $(RS)_3B$. Since triphenylthioborane in its standard state is crystalline, the latent heat of fusion was also required. Enthalpies of fusion of crystalline compounds are usually determined by measuring their heats of solution in an inert solvent. Unfortunately, phenylthioborane was only soluble in those solvents in which complexing occurred. (The heat of solution of triphenylthioborane in 1,4 dioxan was approximately -25 K.cal.mole^{-1}, which is an order of magnitude greater than most enthalpies of solution, indicating that strong Lewis acid-base complexing had taken place). Triphenylthioborane was therefore assumed to have an enthalpy of fusion equal to that of triphenylboron (i.e. 4 K.cal.mole^{-1}). In table IX the heats of formation of the alkylthioboranes and phenylthioborane, in their standard states, are collected together with the mean value of the heat of hydrolysis (ΔH_{obs}).

See TABLE IX

~~Attached~~

A graph of enthalpy of formation of $(RS)_3B$ where R = ethyl, n - propyl, n - butyl and n - amyl in the liquid and gaseous states, versus the number of carbon atoms in $R^{(n)}$ yields a linear relationship. (Fig. I)

TABLE IX.

	$(CH_3S)_3B$	$(C_2H_5S)_3B$	$(n\text{-}C_3H_7S)_3B$	$(n\text{-}C_4H_9S)_3B$	$(n\text{-}C_5H_{11}S)_3B$	$(C_6H_5S)_3B$
$\Delta H_{(obs)} 25^\circ$	-17.6 ± 0.3	-	-22.3 ± 0.3	-23.7 ± 0.3	-24.2 ± 0.3	-21.6 ± 0.3
ΔH_f° (cryst.)	-	-	-	-	-	+15.9 ± 0.9
ΔH_f° (lig.)	-50.3 ± 0.6	-82.8 ± 0.5	-100.8 ± 0.6	-117.1 ± 0.9	-135.7 ± 1.2	-
ΔH_f° (g)	-37.4 ± 0.6	-68.2 ± 0.7	-80.0 ± 0.8	-94.2 ± 1.0	-110.7 ± 1.3	+45.1 ± 1.8

All values are in K.cal.mole^{-1}

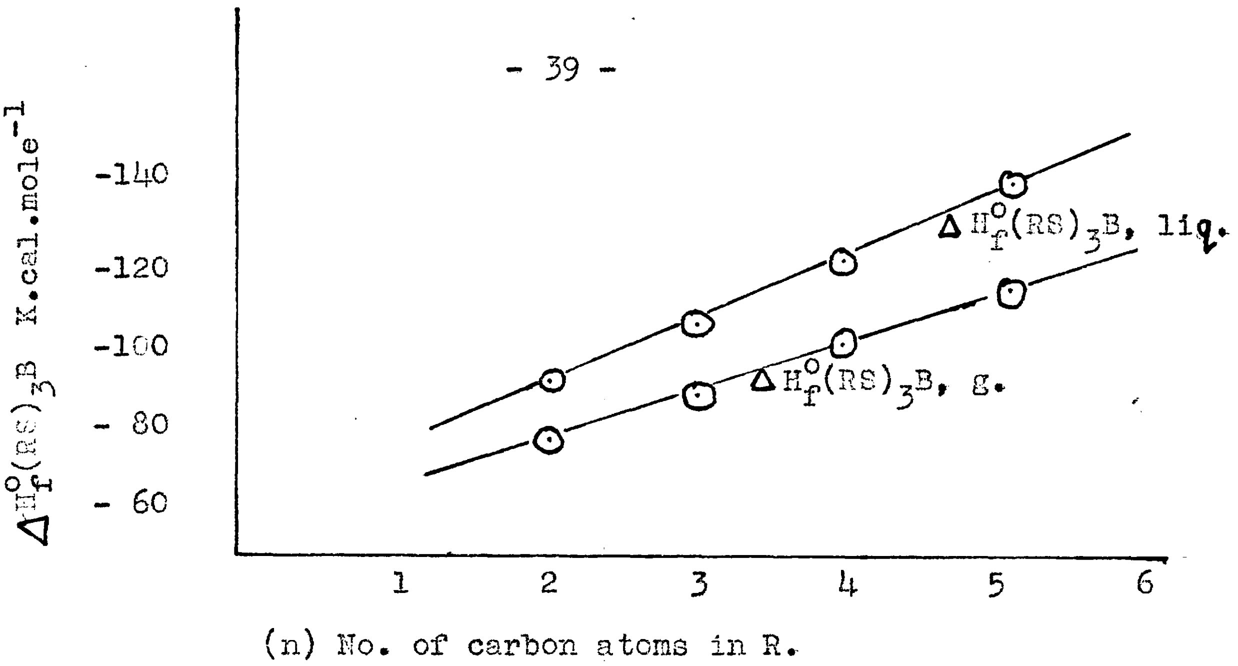


Fig. I

A least squares analysis of the data leads to the following equations for the enthalpies of formation of the trialkylthioboranes

$$-\Delta H_f^o((RS)_3B, liq) = (17.50 \pm 0.12)n + (47.85 \pm 0.44) \text{ K.cal.mole}^{-1}$$

$$-\Delta H_f^o((RS)_3B, g) = (15.11 \pm 0.16)n + (37.49 \pm 0.60) \text{ K.cal.mole}^{-1}$$

Hence the standard heats of formation of the higher homologues ($n = 6, 7....$) may be readily estimated.

The boron-sulphur bond energies in these compounds were evaluated using the measured values of their standard enthalpy of formation (ΔH_f^o,g), the heats of sublimation of the constituent elements (ΔH_f^o atoms) and the equation:

$$\Sigma E = \Sigma \Delta H_f^o \text{ (atoms)} - \Delta H_f^o, g$$

values of the enthalpies of sublimation used in the calculations are tabulated.

TABLE X

Species	ΔH_f^o : 298 (K.cal.gmatom^{-1})	Source
C,g	170.9 ± 0.45	10
H,g	52.10 ± 0.001	10
B,g	132.8 ± 4.0	10
S,g	66.7 ± 0.5	10

Two bond energy schemes were also used.

(1) Laidler-Mackle (L - M)

Numerical values of the bond energies E(C-H), primary, secondary and tertiary and those for $E(C-H)_{ar}$, $E(C-C)_{ar}$ and $E(C_{sp^2}=S)$ were taken from Mackle and Mayrick.(75) Substitution of these values into the above equation yields the boron-sulphur bond energy.

(2) Allen

Application of the Allen scheme to alkyl thioboranes leads to the following expression:

$$\Sigma \Delta H_f^o \text{ (atoms)} - \Delta H_f^o,g = 3B_{cs} + a_2B_{CH} + a_3B_{cc} + 3B_{BS} + a_4\tau_{ccc} + 3\tau_{SBS} + 3\tau_{BSC} + a_5\tau_{ccs} + \Delta^B_{sss}$$

where B is the 'effective' Allen bond energy term, τ and Δ are the magnitudes of the 1, 3 interactions and the interaction of the S_3 trio attached to boron respectively, and a_i are the numbers of such interactions. Using Skinner and Pilcher's(63) collated data (after adjustment to $\Delta H_f^o(S,g) = 66.7$ K.cal.g.atom^{-1} for B_{CH}, B_{CS}, B_{cc}, Γ_{ccc} and Γ_{ccs}, the composite term (W) was evaluated.

$$W = B_{BS} + \Gamma_{SBS} + \Gamma_{BSC} + \tfrac{1}{3}\Delta^{B}_{S'S}$$

Since values of the standard enthalpies of formation of thioethyl and thiomethyl radicals are quoted in literature(75), the mean bond dissociation energy ($\overline{D}$) of the boron-sulphur bond in ethyl and methyl thioborane was also evaluated, from the expression

$$\overline{D}(B-S) = \tfrac{1}{3}(\Delta H_f^o(RS)_3B,g - 3\Delta H_f^o(RS,g) - \Delta H_f^o(B,g))$$

However, the error on these $\overline{D}$ data is too large for the results to be significant.

TABLE XI

R in $(RS)_3B$	E(B-S)(L-M) K.cal.	W(Allen) K.cal.	$\overline{D}$(B-S) from $\Delta H_f^o(RS,g)$K.cal.
CH_3	85.0	87.2	87.4 ± 5
C_2H_5	90.4	91.8	92.5 ± 5
n-C_3H_7	89.4	90.8	
n-C_4H_9	89.3	90.7	
n-C_5H_{11}	89.9	91.3	
C_6H_5	89.8	-	

The error in all bond energies in the second and third columns was ± 1.7 K.cal, except for R = C_6H_5 which was ± 2.5 K.cal. The boron-oxygen bond energy in the corresponding trialkyl borates has been derived(33) from Skinner's data using a similar bond energy scheme. It would be convenient to reproduce these results here. (Table XII).

TABLE XII

Compound	$(CH_3O)_3B$	$(C_2H_5O)_3B$	$(n\text{-}C_3H_7O)_3B$	$(n\text{-}C_4H_9O)_3B$
E(B-O)K.cal	112.4	123.6	124.5	125.1

There is a marked disparity in the boron-sulphur bond energy in methylthioborane and its homologues (~ 5 K.cal.). A corresponding difference also occurs in the trialkyl borates, $(RO)_3B$, (~12 K.cal). If this is due to an inductive effect then it appears that oxygen is more efficient in transmitting this effect than sulphur; arguments based on size support this idea. The fact that the alkylthio-boron bond energy is the same as the arylthioboron bond energy indicates that phenyl substituents do not affect the electronic character of the boron-sulphur bond. Furthermore, it suggests that in the trialkylthioboranes, little or no back-donation from sulphur to boron takes place, because if this was the case the attachment of a phenyl group to sulphur would almost certainly inhibit thisback co-ordination and reduce the boron-sulphur bond strength in triphenylthioborane relative to that in the alkylthioboranes. Support for these conclusions comes from Mackle and Mayrick(75) who investigated the molecules $Ph.CH_2.S.Et$, $Ph.CH_2.S.Me$, $Ph.S.Ph$, and $Ph.S.S.Ph$ thermochemically and found no stabilisation resulting from conjugation between a sulphur atom and an adjacent phenyl group. Thus the order of effectiveness of back co-ordination to a boron atom is now

$$N > O > Cl \geqslant S$$

Bearing in mind the limitations in Skinner's treatment of back-donation to the boron atom, it would be of interest to verify the above sequence for nitrogen and oxygen by the same technique that has been applied to the boron-sulphur compounds, e.g. by evaluating the boron-oxygen and boron nitrogen bond energy in molecules where back co-ordination can take place, and in molecules where it is effectively inhibited (by attachment of phenyl or some other strongly electronegative group to the oxygen or nitrogen atom). A comparison of the B-O bond energy in $(C_6H_5O)_3B$ and $(C_2H_5O)_3B$ molecules, and the B-N bond energy in $(C_6H_5NH)_3B$ and $(C_2H_5NH)_3B$, would yield the π stabilisation energies directly.

SECTION 2. The Thermochemistry of Triphenylboron, Tricyclohexylboron and some phenylboronhalides

Purpose of Investigation

To synthesize the compounds in the series $\text{Ø}_{3-n}BX_n$ where $X = Cl$, Br and $n = 0, 1, 2$ and determine the phenyl-boron bond energy in each. By comparison with the carbon-boron bond energy in tricyclohexylboron to estimate the π character (if any) of the boron-phenyl bond.

Methods of Preparation

There are two main methods available for synthesis of phenylboronhalides and triphenylboron; these are outlined below.

1) Direct Synthesis

Phenylborondichloride and dibromide were first prepared by Michaelis(99) by heating diphenylmercury with boron trihalide in a sealed tube.

$$Hg\text{Ø}_2 + BX_3 \longrightarrow 2\text{Ø}BX_2 + HgX_2$$

Michaelis also prepared the diphenylhalides in a similar manner; diphenylboron chloride was obtained from phenylboron dichloride and diphenylmercury, and diphenylboronbromide from equimolar quantities of diphenylmercury and borontribromide.

$$2\text{Ø}BCl_2 + Hg\text{Ø}_2 \longrightarrow 2\text{Ø}_2BCl + HgCl_2$$

$$Hg\text{Ø}_2 + BBr_3 \longrightarrow \text{Ø}_2BBr + HgBr_2$$

In both cases small yields were noted and phenyl substitution did not proceed beyond this stage. The reaction of phenylmercuric halide with boron trihalide has recently been investigated(94) and shown to give good yields of both phenylboron dichloride and dibromide.

$$\emptyset HgX + BX_3 \xrightarrow[\text{benzene}]{\text{reflux in}} \emptyset BX_2 + HgX_2$$

By refluxing these reagents in toluene for a longer period of time, mainly diphenylboron halides are obtained with a little of the mono-substituted product.(95)

The boronation of benzene to give phenylboron dihalides has been the subject of numerous investigations. Ruigh et al(96) prepared phenylboron dichloride by passing boron trichloride and benzene at 500° - 600°C over palladium metal. Friedel Crafts catalysts have also been used. Muettertles(97) achieved good yields of phenylboron dichloride by heating together benzene and a mixture of boron trichloride, aluminium chloride and methyl iodide, under pressure. Bujwid(81) has obtained 50% conversion from refluxing boron tribromide and benzene in the presence of aluminium bromide

$$\emptyset H + BBr_3 \xrightarrow{AlBr_3} \emptyset BBr_2 + HBr$$

Bowie and Musgrave(98) found that both boron tribromide and boron triiodide react with benzene in the absence of a catalyst when subject to ultraviolet radiation, but no reaction occurred between boron trichloride and benzene under the same conditions. No diphenylboron products were isolated in any of the reactions described above, probably because polysubstitution in the aromatic nucleus is unfavourable due to the strongly electronegative $-BCl_2$ group which deactivates the ring. Generally, the boronation of benzene is not a suitable method for the preparation of phenylboron dihalides, since reaction conditions are severe and the yields are not usually good.

The most convenient method reported so far for the preparation of phenylboron dichlorides is that starting from tetraphenyl tin and boron trichloride.(78) The reaction is relatively fast and the product is obtained in excellent yield.

$$Sn\varnothing_4 + 4BCl_3 \longrightarrow 4\varnothing BCl_2 + SnCl_4$$

There is no evidence that phenylboron dibromide may be similarly prepared.

2) Grignard Reagents

Provide a general method for the attachment of one, two or three aryl groups to boron. The Grignard reagent is added to boron trifluoride in ether solution.

$$\varnothing MgBr + BF_3/\text{etherate} \longrightarrow \varnothing BF_2 \xrightarrow{2H_2O} \varnothing B(OH)_2 + 2HF$$

boron trichloride and bromide have also been used, but to a lesser extent. The trialkylborates $(RO)_3B$ have been widely employed in place of trihalides. Generally the intermediate halide or alkyl ester is not isolated but is hydrolysed to the corresponding acid. Phenylboron halide derivatives may be obtained from the Grignard product in two ways. By dehydration of the acid to give the anhydride, which is then converted in good yield to the corresponding phenylboron halide by reaction with boron trihalide according to Gerrard's procedure.(82)

$$(\emptyset_2B)_2O + BX_3 \longrightarrow 2\ \emptyset_2BX + BOX$$

$$\emptyset BO + BX_3 \longrightarrow \emptyset BX_2 + BOX$$

Phenylboron halides may be alternatively prepared by attachment of three aryl groups to boron followed by the stepwise replacement of these by halogen (using BX_3 or HX).

The reaction of phenyl lithium with trialkyl borates has also been used to arylate boron. As in the case of the Grignard reaction, phenylboronic and borinic acids are isolated as products.

The compounds used in this investigation were prepared by the following methods. Phenylboron dichloride was synthesized from tetraphenyl tin and boron trichloride. This method has been further developed in this laboratory and both diphenylboron chloride and triphenylboron have been prepared in reasonable yields. Thus, after removal of stannic chloride (by distillation) from the initial preparation, tetraphenyl tin was added according to the equation

$$Sn\emptyset_4 + 4\emptyset BCl_2 \longrightarrow 4\emptyset_2BCl + SnCl_4$$

diphenylboron chloride could be separated by vacuum distillation and was obtained in about 50% yield. Alternatively the addition of a further amount of tetraphenyl tin to the above reaction mixture and distillation of the products gave triphenylboron (40% yield after recrystallisation from diethyl ether).

Phenylboron dibromide was prepared by the simple displacement reaction

$$\emptyset BCl_2 + BBr_3 \longrightarrow \emptyset BBr_2 + BCl_3$$

by mixing phenylboron dichloride and boron tribromide at -80°, followed by removal of boron trichloride. The reaction of diphenylborinic anhydride with boron bribromide in methylene chloride yielded diphenylboron bromide, which was purified by vacuum distillation after removal of the solvent.

$$(\emptyset_2B)_2O + BBr_3 \longrightarrow 2\emptyset_2BBr + BOBr$$

Tricyclohexylboron had already been prepared in this laboratory from triethylamineborane and cyclohexene.(83) The detailed preparation and analysis of these compounds is given in experimental section 3.

<u>Calorimetry</u>

<u>Phenylboron halides</u> hydrolyse rapidly and quantitatively to phenylboronic acid and hydrogen halide.

$$\emptyset BX_2 + 2H_2O \longrightarrow \emptyset B(OH)_2 + 2HX$$

Sometimes the hydrolysis occurred violently, causing the calorimetric fluid to be splashed on the sides of the calorimeter. An attempt was made to subdue the reaction by a technique which Skinner(18) applied to the ethoxychloroboron compounds, i.e. by dilution of the reactant with carbon tetrachloride. This, however, was not successful because carbon tetrachloride coated the phenylboronic acid produced and prevented its further dissolution. It was found by reducing the amount of sample and increasing the volume of calorimetric fluid (125 ml to 150 ml water), that the reaction proceeded without undue violence. The weight of sample was also selected such that phenyl boronic acid remained in solution, since this acid has a small aqueous solubility (17g/litre).

$$\emptyset BX_2 \text{ (liq)} + (n + 2)H_2O \text{ (liq)} = (\emptyset B(OH)_2 + 2HX)nH_2O \ldots. \quad \Delta H_{obs}.$$

Hence

$$\Delta H_f^o(\emptyset BX_2, \text{ liq}) = \Delta H_f^o(\emptyset B(OH)_2 \text{ aq}) + 2\Delta H_f^o(HX(\tfrac{n}{2}H_2O)) - 2\Delta H_f^o(H_2O, \text{ liq}) - \Delta H_{obs}$$

Both phenylboron dibromide and diphenylboron chloride (studied later) have melting points close to 25°. Liquid $\emptyset_2BCl$ could be supercooled to 25°C and hence the thermodynamic data for this compound refer to the metastable liquid; but phenylboron dibromide did not supercool and was studied in the liquid state at 30°. It was assumed that the difference in ΔH_{obs} at 25° and 30° within the limits of error, so these data apply to the hypothetical liquid state at 25°C. The assumption is probably justified as an isolated observation of the heat of hydrolysis of $Ø_2BCl$ at 30°C was only marginally different from observations at 25°C.

Calculation of the standard heat of formation of the phenylboron dihalides requires a knowledge of the enthalpy of formation of phenylboronic acid. This datum has recently been determined(39) in this laboratory via the oxidation of phenylboronic acid with aqueous hydrogen peroxide in basic solution.

$$ØB(OH)_2 + H_2O_2 \longrightarrow ØOH + H_3BO_3$$

The ancillary data used to calculate ΔH_f^o $ØBX_2$ are collected in Table XV. Values of the standard enthalpy of formation of phenylboron dichloride and dibromide are reported in Table XIII together with the observed heats of hydrolysis.

Table XIII

	ΔH_{obs}(K cal.mole^{-1})	N	ΔH_f^o25°(K cal.mole^{-1}
$ØBCl_2$, liq	-40.3 ± 0.3 (25°)	2900	-71.9 ± 0.6
$ØBBr_2$, liq	-48.8_5 ± 0.2 (30°)	4800	-41.6 ± 0.6

Diphenylboron halides

These compounds hydrolyse quantitatively and rapidly but not violently, according to the equation

$$\emptyset_2BX + H_2O \longrightarrow \emptyset_2BOH + HX$$

Diphenylborinic acid is a slightly water soluble, intractable oil which decomposes on standing.(100) Hydrolyses were carried out under a nitrogen atmosphere and in saturated solutions of the acid, so that the diphenylborinic acid produced can be assumed to be in its standard state (s.s.) even though this state is ambiguous. It was assumed that the thermal effect due to further dissolution (or precipitation) as the reaction proceeded was negligible. Independant experiments have shown that the slow decomposition of the acid was not thermally detectable.

$$\emptyset_2BX(liq) + (n + 2)H_2O(liq) = \emptyset_2BOH(ss) + HX.nH_2O \ldots \Delta H_{obs}$$

equating standard enthalpies of formation

$$\Delta H_f^o(\emptyset_2BX,liq) = \Delta H_f^o(\emptyset_2BOH,ss) + \Delta H_f^o(HX.nH_2O) - \Delta H_f^o(H_2O,liq) - \Delta H_{obs}$$

Although the standard heat of formation of diphenylborinic anhydride has been determined, the heat of formation of the acid has not (because of the unstable nature of the acid). It was, however, estimated(39) in the following manner: for the reaction

$$(\emptyset BO)_3(cryst) + 3H_2O(liq) = 3\emptyset B(OH)_2(cryst) \ldots \Delta H = -9.8 \pm 2.8 \text{ K.cal.mole}^{-1}$$

In the gas phase this hydration process was interpreted in terms of breaking three B - O bonds in the anhydride, three O - H bonds in water and the subsequent reformation of these six bonds in three moles of acid. The corresponding hydration process for diphenylborinic anhydride:

$$(\emptyset_2B)_2O(\text{cryst}) + H_2O(\text{liq}) = 2\emptyset_2BOH\ (\text{ss})$$

involves only one O - H and B - O bond, hence it was assumed that the enthalpy of hydration of phenylboronic anhydride was three times that of phenylborinic anhydride. This gives

$$\Delta H_f^o(\emptyset_2BOH,\ \text{hypothetical crystalline state}) = \sim\ -78\ \text{K.cal.mole}^{-1}.$$

Because of the uncertainty of the above value, it was decided to determine $\Delta H_f^o(\emptyset_2BOH, ss)$ by an indirect method. Diphenylboron chloride was oxidised in a mixture of 0.1 M hydrogen peroxide and 0.1 M sodium hydroxide (this mixture is hereafter termed aqueous excess base (a.e.b.)). Kuivila(101) has studied the kinetics of the oxidation of the boron-phenyl bond (in phenylboronic acid) and has shown that this reaction, to give phenol and boric acid, is rapid and quantitative. Hence for diphenylboron chloride (supercooled to 25°) the reaction is

$$\emptyset_2BCl(\text{liq}) + 2H_2O_2(\text{a.e.b.}) + NaOH(\text{aq}) = \overset{2\phi OH}{\cancel{2\emptyset H}}(\text{a.e.b.}) + NaCl(\text{aq})$$
$$+ H_3BO_3(\text{a.e.b.})\ldots\ \Delta H_{obs}$$

$$\Delta H_f^o(\emptyset_2BCl,\text{liq}) = \Delta H_f^o(H_3BO_3,\text{a.e.b.}) + \Delta H_f^o(NaCl.\text{aq}) +$$
$$2\,\Delta H_f^o(\emptyset OH,\text{a.e.b.}) - 2\,\Delta H_f^o(H_2O_2(\text{a.e.b.})) - \Delta H_f^o(NaOH,\text{aq}) - \Delta H_{obs}$$

Since all the values of the terms on the right hand side of this equation are known (Table XV[illegible]), the standard enthalpy of formation of diphenylboron chloride (liq) may be evaluated. Insertion of this value into the above expression for the hydrolysis of $\emptyset_2BCl$ (liq) gives $\Delta H_f^o(\emptyset_2BOH, ss) = -77.6 \pm 1.8$ K.cal.mole^{-1}, in good agreement with the estimated figure.

TABLE XIV

The enthalpies of hydrolysis and formation of diphenyl boron chloride and diphenylboron bromide

	N	ΔH_{obs} 25°(K.cal.mole^{-1})	ΔH_f^o 25°(K.cal.mole^{-1})
$\emptyset_2BCl$(liq)	2000	$-17.2_5 \pm 0.1$	-32.1 ± 1.8
$\emptyset_2BBr$(liq)	1700	-22.0 ± 0.4	-16.3 ± 1.8

Triphenylboron and tricyclohexylboron

The basic oxidising medium (a.e.b.) used for diphenyl boron chloride was also employed in the case of triphenylboron and tricyclohexylboron. Oxidative hydrolysis thus yielded phenol (or cyclohexanol) and boric acid quantitatively. The initial experiments with these compounds were unsuccessful in that, following ampoule fracture the compound floated and hydrolysis continued over periods of 30 minutes or more. This type of calorimeter is not suitable for slow reactions because of the large error involved in the back extrapolation procedure. In subsequent experiments triphenylboron was dissolved in 1,4 dioxan and tricyclohexylboron in cyclohexanol, then hydrolyses were complete within a few minutes. (Tricyclohexylboron was soluble in hot 1,4 dioxan but crystallised from this solvent on cooling). Both solvents were distilled (dioxan from sodium) immediately prior to use.

For triphenylboron we may write the equation:

$$\text{Ø}_3\text{B(dioxan sol}^{\text{n.}}) + 3H_2O_2\text{(a.e.b.)} = (3\text{ØOH} + H_3BO_3)\text{a.e.b./dioxan} \ldots\ldots\ \Delta H_{obs}.$$

The following ancillary data were also determined:

$$\text{dioxan (liq)} + \text{a.e.b.} = \text{dioxan/a.e.b.} \ldots\ldots\ \Delta H_1$$

$$\text{Ø}_3\text{B(cryst)} + \text{dioxan} = \text{Ø}_3\text{B(dioxan sol}^{\text{n.}}) \ldots\ \Delta H_3$$

The observed heat of reaction ΔH_{obs} (in cals) may be expressed as the sum of two components, (i) the heat change (ΔH_1) due to the solution of dioxan in a.e.b.; (ii) the heat change (ΔH_2) due to the reaction of triphenylboron in a.e.b.

$$H_{obs} = N_1\ \Delta H_1 + N_2\ \Delta H_2$$

where N_1 and N_2 are the numbers of moles of dioxan and triphenylboron respectively.

Hence

$$\Delta H_f^o\text{Ø}_3\text{B(cryst)} = \Delta H_f^o(\text{Ø}_3\text{B, dioxan sol}^{\text{n.}}) - \Delta H_3 =$$
$$\Delta H_f^o(H_3BO_3,\text{a.e.b.}) + 3\Delta H_f^o(\text{ØOH,a.e.b.}) - 3\Delta H_f^o(H_2O_2,\text{a.e.b.})$$
$$- \Delta H_{obs} - N_1\Delta H_1 - \Delta H_3$$

The enthalpy of solution of $\text{Ø}_3\text{B}$ in a non-polar solvent (benzene) was also measured to obtain an estimate of the enthalpy of fusion of $\text{Ø}_3\text{B}$.

$\Delta H_{soln.}(\emptyset_3B$ in dioxan$) = \Delta H_3 = 3.3 \pm 0.13$ K.cal.mole^{-1}

$\Delta H_{soln.}(\emptyset_3B$ in benzene$) = 4.1 \pm 0.2$ K.cal.mole^{-1}

$\Delta H_{soln.}($dioxan in a.e.b.$) = \Delta H_1 = -2.28 \pm 0.01$ K.cal.mole^{-1}

$\underline{\Delta H_f^o\ \emptyset_3B(\text{cryst})\ 25^o = 11.6 \pm 1.9\ \text{K.cal.mole}^{-1}}$

Tricyclohexylboron was oxidatively hydrolysed as a cyclohexanol solution in basic oxidising medium

$(C_6H_{11})_3B$ (cyclohexanol sol$^{n.}$) + $3H_2O_2$(a.e.b.) = $(3C_6H_{11}OH$ +
$H_3BO_3)$ a.e.b./cyclohexanol ...... ΔH_{obs}

The following data were determined:

$(C_6H_{11})_3B$(cryst) + cyclohexanol = $(C_6H_{11})_3B$(cyclohexanol sol$^{n.}$) ..... ΔH_3

cyclohexanol (liq) + a.e.b. = cyclohexanol/a.e.b...... ΔH_1

$$\Delta H_{obs} = N_1 \Delta H_1 + N_2 \Delta H_2$$

where ΔH_2 is the enthalpy of reaction of tricyclohexylboron in a.e.b., N_1 and N_2 are the number of moles of cyclohexanol solvent and tricyclohexylboron respectively.

$\Delta H_f^o((C_6H_{11})_3B,\text{cryst}) = \Delta H_f^o((C_6H_{11})_3B,\ \text{cyclohexanol}) - \Delta H_3$
$= 3\,\Delta H_f^o(C_6H_{11}OH,\text{a.e.b.}) + \Delta H_f^o(H_3BO_3,\text{a.e.b.}) - 3\,\Delta H_f^o$
$(H_2O_2\ \text{a.e.b.}) - \Delta H_{obs} + N_1 \Delta H_1 - \Delta H_3$

ΔH solution $((C_6H_{11})_3B$ in cyclohexanol$) = \Delta H_3 =$
1.9 ± 0.3 K.cal.mole^{-1}

$\Delta H_{soln.}($cyclohexanol in a.e.b.$) = \Delta H_1 = -1.98 \pm 0.3$ K.cal.mole^{-1}

$\underline{\Delta H_f^o((C_6H_{11})_3B,\text{cryst})25^oC = -115.3 \pm 2.5\ \text{K.cal.mole}^{-1}}$

TABLE XV

Species	ΔH_f^o 25°(K.cal.mole^{-1})	Source
$\emptyset B(OH)_2(aq)$	-168.8 ± 0.5	39
H_2O (liq)	-68.32	69
HCl.3000 H_2O	-39.96	102
HBr.3000 H_2O	-29.05 ± 0.09	102
H_3BO_3 (aq)	-256.5 ± 0.2	72
$\emptyset OH$ (cryst)	-39.46 ± 0.08	103
$C_6H_{11}OH$ (liq)	-83.45	104
H_2O_2 (aq)	-45.68	69
NaCl.14,000 H_2O	-97.27	69
NaOH.500 H_2O	-112.12	69

The enthalpies of solution of phenol (cryst) and boric acid (cryst) used were -4.40 ± 0.1 and -5.26 ± 0.04 K.cal.mole^{-1} respectively. The heat of solution of hydrogen peroxide and sodium chloride in aqueous excess base was assumed to be equal to that of water.

Enthalpies of transition

The two methods used to measure the latent heats of vaporisation of these compounds have been outlined in section 4, of the experimental. In the case of phenylboron dichloride a static method wasused and for the rest of the compounds a dynamic distillation technique. Experimental data are represented in the form

$$\log_{10}P\ (\mathrm{mm}) = a - \frac{b}{(T^{o}K)}$$

where a and b are constants obtained from a least squares analysis. Heats of vaporisation have been 'corrected' to 25°C using Watson's equation (see experimental section 4). These data are now collected in Table XVI.

TABLE XVI

Compound	Range °C	a	$10^{-3}b(^{o}K)$	ΔH^{T}_{vap}	ΔH^{298}_{vap}
ϕBCl_2	0-45	6.29	1.76	-	8.05
ϕ_2BCl	90-212	6.48	2.17	9.9	10.8
ϕBBr_2	118-160	7.63	2.30	10.5	11.7
ϕ_2BBr	163-243	8.35	3.15	14.4	16.5
ϕ_3B	150-295	8.28	3.36	15.4	18.6

All enthalpies of vaporisation are in K.cal.mole^{-1} and the error is the same in each case, i.e. ± 0.2 K.cal.mole^{-1}. Combination of the above results with the data from Tables XIII, XIV and XVI yields values of the enthalpy of formation of these compounds in the crystalline, liquid and gaseous states. These are summarised in Table XVII.

TABLE XVII

	$\text{Ø}BCl_2$	Ø_2BCl	$\text{Ø}BBr_2$	Ø_2BBr	Ø_3B	$(C_6H_{11})_3B$
$\Delta H^o_{f(cryst)}25^o$	-	-	-	-	$+11.6\pm1.9$	-115.3 ± 2.5
$\Delta H^o_f(liq)25^o$	-71.9 ± 0.6	-32.1 ± 1.5	-41.6 ± 1.5	-16.3 ± 1.5	-	-
$\Delta H^o_f(g)25^o$	-63.8 ± 0.6	-21.3 ± 1.5	-29.9 ± 0.6	$+ 0.2\pm1.5$	$+34.3\pm1.9$	-95.8 ± 2.7*

All values are in $K.cal.mole^{-1}$

* Assuming enthalpy of sublimation Ø_3B = enthalpy of sublimation $(C_6H_{11})_3B$.

Free Energies of Reaction

It has already been mentioned at the beginning of this section that boronation of benzene was not a good preparative method for phenylboron dihalides. The thermodynamic feasibility of this reaction may now be assessed.

$$ØH(g) + BX_3(g) \longrightarrow ØBX_{2(g)} + HCl(g)$$

Lockhart(25)(112) has derived free energy functions for both phenylboron dichloride and bromide from a vibrational analysis and using a rigid rotator simple harmonic oscillator approximation. (Molecular parameters for $ØBBr_2$ are guessed from $ØBCl_2$ and BBr_3). Free energies of formation and reaction of $ØBCl_2$ and $ØBBr_2$ at 25° and 500°C are listed in Table XVIII.

TABLE XVIII

	$\Delta G_f^o(g)25^o$	$\Delta G_f^o(g)500^o$	ΔHreaction 25^o	ΔG reaction 25^o	500^o
X = Cl	-55.1±0.7	-19.3	-9.3	-8.2	-7.5
X = Br	-28.8±0.8	- 0.7	-9.1	-8.6	-15.5

(all data in $K.cal.mole^{-1}$ with an error of about ± 1 $K.cal.mole^{-1}$)

Increase in temperature has little effect on the formation of phenylboron dichloride but favours the formation of phenylboron dibromide, although at elevated temperature this molecule is marginally stable with respect to the decomposition to its elements. It was also noted that disubstitution in the benzene nucleus did not take place in any of these boronation reactions:

$$\text{ØBX}_{2(g)} + \text{ØH(g)} \longrightarrow \text{Ø}_2\text{BX(g)} + \text{HX(g)}$$

Using the standard enthalpy of formation data in Table XVII the heats of reaction for X = Cl and X = Br at 25^{o} were evaluated as 0.7 ± 1.5 and 1.6 ± 1.5 K.cal.mole^{-1} respectively. Thus, in agreement with experimental observations, formation of diphenyl boron halides by the above reaction is not favourable.

Disproportionation of phenylboron halides

McCusker and Bright(113) have studied the relative disproportionation tendencies of the alkylboron halides, and found alkylboron bromides are significantly different from the corresponding alkylfluoro and alkylchloro compounds. Whereas alkylboron dibromides undergo a slow thermal disproportionation to boron tribromide and trialkylboron, the dichloro and difluoro compounds are completely resistant to disproportionation under the same conditions.

$$2RBr_2 \longrightarrow BBr_3 + R_2BBr$$

On the other hand, of the three dialkylhalo compounds, dialkylboron bromides show the smallest tendency towards disproportionation

$$2R_2BX \longrightarrow R_3B + RBX_2$$

$$R_2BF < R_2BCl < R_2BBr \text{ (increasing stability)}$$

The differences in disproportionation behaviour were shown to be due to thermodynamic rather than kinetic factors. If it is assumed that thermodynamic factors also control the thermal decomposition of phenylboron halides and that they disproportionate to give similar products, their relative disproportionation tendencies may be predicted from the data in Table XVII.

$$2\phi BX_{2(g)} \longrightarrow BX_{3(g)} + \phi_2BX(g)$$

$X = Cl$ ΔH (reaction) $25^\circ = 8.8 \pm 1.6$ K.cal.mole^{-1}

$X = Br$ ΔH (reaction) $25^\circ = 10.3 \pm 1.6$ K.cal.mole^{-1}

Thus, in both cases, decomposition to the above reaction products is unlikely to occur and furthermore ϕBCl_2 and ϕBBr_2 will possess approximately equal stability with respect to this disproportionation.

$$2\phi_2BX_{(g)} \longrightarrow \phi_3B(g) + \phi BX_{2(g)}$$

$X = Cl$ ΔH (reaction) $25^\circ = 13.1 \pm 2.5$ K.cal.mole^{-1}

$X = Br$ ΔH (reaction) $25^\circ = 4.1 \pm 2.5$ K.cal.mole^{-1}

Again, the above decomposition of diphenylboron halides is unlikely to occur, but if it does then diphenyl boron chloride will disproportionate to a smaller extent than diphenylboron bromide, i.e. diphenylboron chloride will be more stable than the bromide, which is the reverse of the order observed for dialkyl boron halides.

The ancillary data used in these calculations was taken from ref. 69.

Bond Energies and Molecular Structure

In order to calculate the carbon-boron bond energy in the compounds studied, the standard enthalpy of formation of the phenyl radical ($\Delta H_f^o\text{Ø}(g)$) must be known. It may be derived from the equation

$$\Delta H_f^o\text{Ø}(g) = D(\text{Ø} - H) - \Delta H_f^o H(g) - \Delta H_f^o \text{Ø}H(g)$$

The standard heats of formation of atomic hydrogen and gaseous benzene are accurately known, but the phenyl-hydrogen bond dissocation energy varies considerably. Some of the data obtained by several different methods are listed in Table XIX.

TABLE XIX

$D(\text{Ø} - H)$ K.cal.	Method	Source
101.9 ± 3	Kinetic	105
107.0 ± 3	Electron impact	106
105.6 ± 2	Electron impact	107
104.2 ± 1.7	Kinetic	108
103.1 ± 2.7	Kinetic	108

The mean of these data (104.4 ± 1.7 K.cal.) and an error of four times the standard deviation has been used here. This gives $\Delta H_f^o\text{Ø}_{(g)} = 72.1 \pm 1.7$ K.cal.mole^{-1} and is in agreement with a 'best value' selected recently.(109) However, it should be mentioned that in a paper presented to the American Chemical Society Meeting in April 1967, S.W. Benson, D.M. Golden and A.S. Rodgers gave a value for the bond dissociation energy of the phenyl-hydrogen bond = 112.3 ± 1 K.cal, which they obtained from equilibrium measurements. This makes $\Delta H_f^o\phi(g) = 80.0 \pm 1$ K.cal. mole^{-1}; a value which is considerably greater than the figure quoted above. Since, however, this is an isolated observation and because it differs markedly from the majority of other determinations, we have preferred to disregard it in favour of the above mean value. The standard enthalpy of formation of the cyclohexyl radical ($\Delta H_f^o\ C_6H_{11}(g) = 12 \pm 3$ K.cal.mole^{-1}) was taken from reference 109. Carbon-boron bond energies were calculated using these values, the data from Table XVII and the following thermochemical cycle.

$$\begin{tikzcd}
\phi_{3-n}BX_n(g) \arrow[rr, "(3-n)E(B-\phi) + nE(B-X)"] & & (3-n)\phi_{(g)} + B_{(g)} + nX_{(g)} \\
& (3-n)(6C\ (\text{graphite}) + \frac{5}{2}H_2(g)) + \frac{n}{2}X_2(g\ \text{or liq}) + B\ (\text{cryst}) \arrow[ul, "\Delta H_f^o\ \phi_{3-n}BX_n(g)"] \arrow[ur, "(3-n)\Delta H_f^o\phi_{(g)} + \Delta H_f^oB_{(g)} + n\Delta H_f^oX_{(g)}"'] &
\end{tikzcd}$$

hence

$$(3-n)\ E(B-\phi) = \Delta H_f^o\ \phi_{3-n}BX_n(g) + (3-n)\Delta H_f^o\phi_{(g)} + \Delta H_f^oB(g) + \Delta H_f^oX(g) - nE(B-X)$$

E(B-C) in tricyclohexylboron is readily obtained by substituting C_6H_{11} for Ø and putting n = 0 in the above equation. (Strictly speaking, E(B-C) in tricyclohexylboron is the mean bond dissociation energy $\bar{D}$(B-C); similarly E(B-Ø) in triphenylboron is $\bar{D}$(B-Ø). But the bond energy terms are retained to avoid complicating the text). The ancillary data used in calculations is collected in Table XX.

TABLE XX

Species	ΔH_f^o K.cal.mole^{-1}	Source
$H_{(g)}$	52.1	10
$ØH_{(g)}$	19.82	110
$B_{(g)}$	132.8 ± 4	10
$Br_{(g)}$	26.74	10
$Cl_{(g)}$	28.94	10

It was assumed that the boron-halogen bond energies in the arylboron halides are equal to those in boron trihalides (using data from ref. 10, E(B-Cl) = 105.3 ± 1.3 K.cal. and E(B-Br) = 87.3 ± 1.3 K.cal.). This assumption is probably justified (at least for the phenylboron chlorides), since in these compounds the boron-chlorine bond length varies little with environmant.(111)(e.g. B-Cl in BCl_3 = 1.73 ± 0.02Å, and B-Cl in $ØBCl_2$ = 1.72 ± 0.03Å). There is no corresponding data for the bromoderivatives.

Values of the carbon-boron bond energies (in K.cal.) are given in Table XXI.

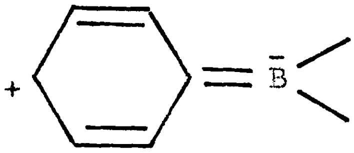
TABLE XXI

	$\emptyset BCl_2$	$\emptyset_2BCl$	$\emptyset BBr_2$	$\emptyset_2BBr$	$\emptyset_3B$	$(C_6H_{11})_3B$
E(B-C)	116.0±2.3	110.4±2.3	113.7±2.3	108.3±2.3	104.9±2.3	88.2±3.4
$E(B-C)_\pi$	28	22	26	20	17	-

The π contribution to the boron-phenyl bond energy was derived from the expression:

$E(B-C)_\pi = E(B-C)$ in $\emptyset_{3-n}BX_n$ - $E(B-C)$ in$(C_6H_{11})_3B$.

Hence it appears that the boron-phenyl bond in phenylboron halides is strongly resonance stabilised. (Benson's figure for $\Delta H_f^o \emptyset_{(g)}$ will increase the above values of $E(B-C)_\pi$ by ~8 K.cal.; the relative magnitudes will remain the same, however.) This stability can be attributed to structures of the type:



Resonance stabilisation of this type is not an uncommon feature of organometallic systems, as is shown in Fig.II.

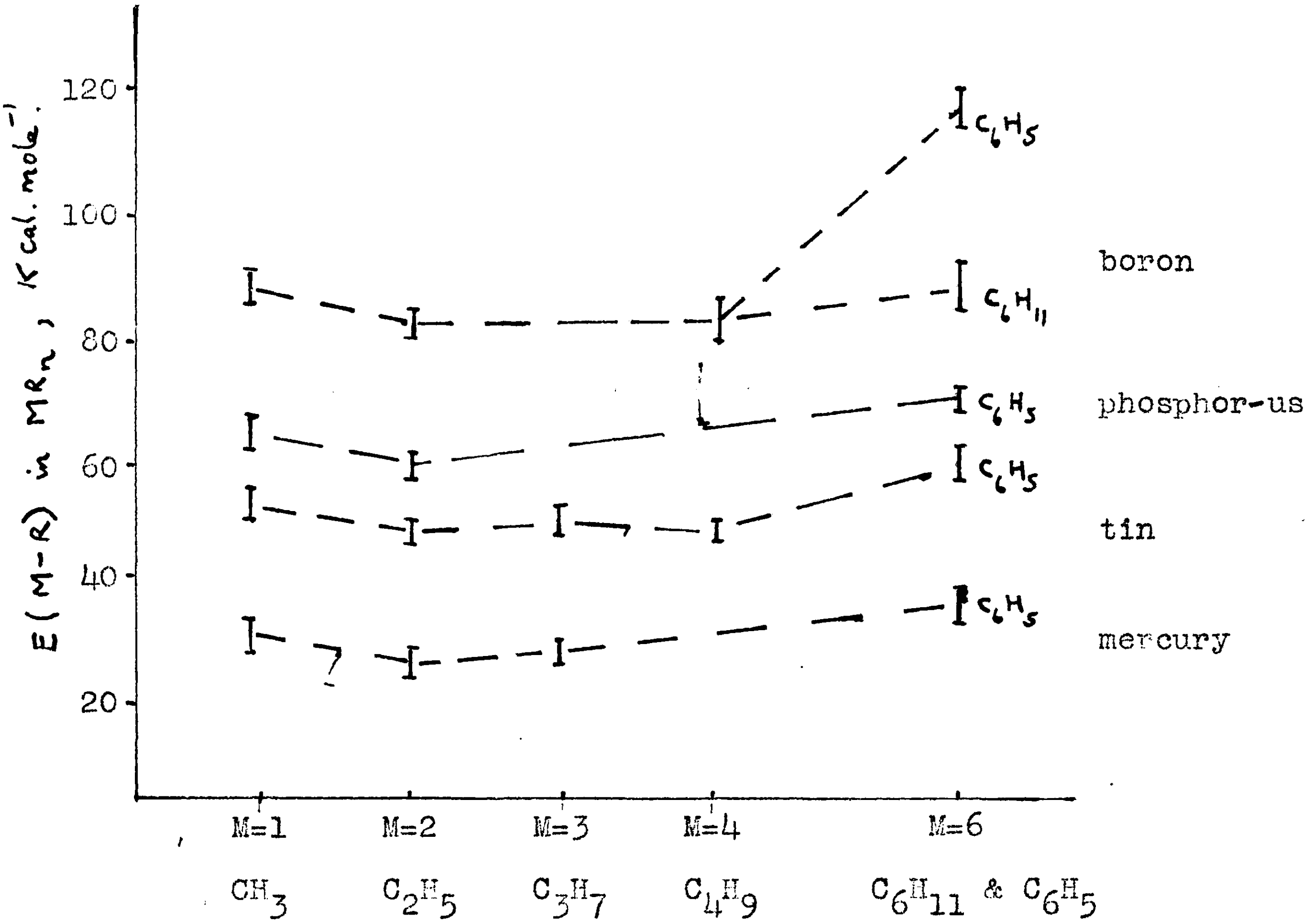


Fig.II Variation in bond energy E(M-R) in MR_n with number of carbon atoms in R (m)

This estimate of the magnitude of the π contribution to the phenyl-boron bond falls between two other values. Lockhart(25)(112 has estimated the barrier to boron-phenyl rotation in ϕBCl_2 (C_{2v} planar) from a knowledge of torsional modes and the reduced moment of inertia as ~ 45 K.cal., and that in ϕBBr_2 (probably C_{2v} planar) as 37 K.cal. In this work it has been assumed that the σ contribution to the E(B-C) bond is 88 K.cal, from which values of 28 and 26 K.cal. are obtained for $E(B-C)_{\pi}$ in $\emptyset BCl_2$ and $\emptyset BBr_2$ respectively. A simple Hückel molecular orbital treatment(114) of several triarylborons indicates the resonance stabilisation for a coplanar system to be 12 K.cal., i.e. 4 K.cal. per boron-phenyl bond.

However, to compare the σ contribution of a C_{sp2}- B bond with the bond energy of a $C_{sp}3$-B bond may not be quite justified. Indeed, in a molecule such as tetraphenyl tin, where the enhancement is ~ 15 K.cal. per phenyl-tin bond, it is unlikely that resonance would contribute to stabilisation due to the steric requirements of the phenyl group and the fact that tin is tetrahedrally co-ordinated. Thus it is also possible that the bond strength enhancement in boron aryls relative to boron alkyls is a combination of both σ and π effects, or even a pure σ effect.

From the data in Table XXI, the boron-phenyl bond decreases in strength with successive phenyl substitution. This may now be interpreted in terms of molecular configuration.

<u>Phenylboron dihalides</u>. Phenylboron dichloride (and, by analogy, phenylboron dibromide) is found to be planar by electron diffraction(22) and in this configuration, resonance stabilisation is a maximum. The difference in $E(B-C)_{\pi}$ between $\emptyset BCl_2$ and $\emptyset BBr_2$ is not significant compared to the

accuracy of the data. This is in line with Perkins' observations(28), who investigated the π electronic structures of these molecules by a molecular orbital self-consistant field technique, that the bond order of B-C in $\emptyset BCl_2$ and $\emptyset BBr_2$ is about the same. In contrast, however, to the above results, Perkins considered that electron density on the boron atom originated mainly from the halogen π orbitals and that contributed by the phenyl ring to boron was small.

Diphenylboron halides. In both diphenylboron chloride and diphenylboron bromide the π stabilisation is decreased by ~6 K.cal. This is probably because the phenyl rings are twisted out of the BC_2X plane in order to reduce ring-ring steric interaction at the expense of resonance stabilisation.

Triphenylboron. In this molecule the π stabilisation energy of the boron-phenyl bond is further decreased (~ 11 K.cal.), suggesting that the phenyl groups are twisted at an even greater angle from the trigonal plane than in the diphenylboron halides. There is some experimental evidence to justify this interpretation. Ramsey(115) has investigated the ultraviolet spectra of triphenylboron and some substituted triarylboron compounds (tri-p-tolyl-, trimesityl-, and tri-1-naphthylboron) in methylcyclohexane solution. All these compounds show a broad long-wavelength absorption which Ramsey attributed to an intramolecular charge-transfer transition from the aromatic ring to the boron empty P-orbital. He observed a progressive decrease of the molar extinction coefficient in going from triphenylboron to trimesitylboron. Thus, the increased angle of twist from the BC_3 plane, corresponding to the increased steric requirements of the phenyl groups, decreases the overlap between donor and acceptor orbitals. Ramsey also observed that the broad wavelength absorption consisted of at least two or three overlapping transitions. One possible explanation of this is that not all of the rings in the triphenylboron molecule are identical. It has been necessarily assumed in deriving the π stabilisation energy that all three B-phenyl bonds in triphenylboron (gaseous) are equivalent. But, assuming that the BC_3 skeleton is planar, there are three ways in which the phenyl groups may be arranged. These are: (i) each ring could be inclined at an equal angle to the trigonal plane (symmetrical propeller configuration), (ii) two phenyl groups could be inclined at one angle and the third at a different angle, (iii) all rings could be inclined at different angles to the plane.

The triphenylmethyl cation (Ø_3C^+) was assigned(116) the symmetrical propeller configuration on the basis of infrared evidence. Since this cation is isoelectronic with triphenylboron it is probable that structure (i) is correct.

Weismann and Schug(114) have examined tri-p-tolylboron and several other methyl substituted triarylborons from a theoretical standpoint (they consider only structure (i) for tri-p-tolylboron). These workers calculated the net potential energy of the molecules by assuming a rigid σ skeleton and summing all the non-bonded interactions and the resonance energy. The resonance energy was expressed as a function of the angle of twist ($90^{\circ} - \tau$) of a phenyl group from the trigonal plane. As the ligands approach a vertical position to the plane ($\tau \rightarrow 0^{\circ}$) the ortho hydrogen atoms eclipse one another, and at the other extreme where $\tau \rightarrow 90^{\circ}$, the hydrogen atoms overlap with the ring carbon atoms of the other ligands. From considerations of interatomic distances, Weismann and Schug showed that the limits of the angle τ were: $25^{\circ} < \tau \leq 70^{\circ}$. For tri-p-tolylboron they deduced an equilibrium configuration with $\tau \sim 45^{\circ}$, when the resonance contribution (proportional to s in τ), had decreased $\sim$ 35% from the maximum value. Assuming triphenylboron has the same configuration, then 11 K.cal. ($E(B\text{-}C)_{\pi}$ in $\text{Ø}BCl_2$ - $E(B\text{-}C)_{\pi}$ in Ø_3B) represents a 35% decrease in resonance stabilisation giving a total resonance energy of $\sim$ 30 K.cal. This is in reasonable agreement with that observed. ($\sim$ 28 K.cal.)

Hence, it seems probable that triphenylboron in the gaseous phase has a symmetrical propeller configuration in which each phenyl group is twisted $\sim 45^\circ$ from the BC_3 plane.

The X-ray crystallographic structure of triphenylboron

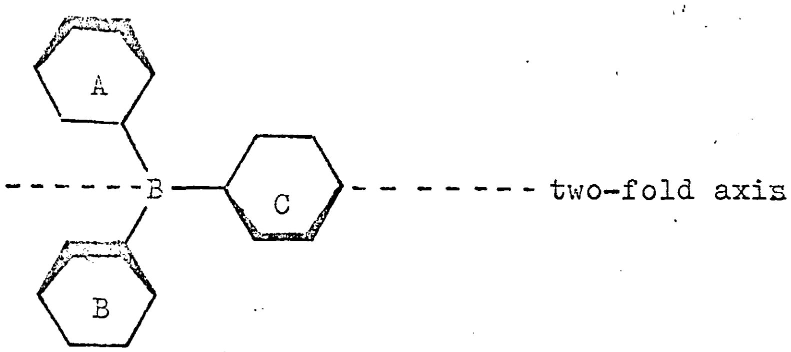
An **X**-ray crystallographic study of triphenylboron has been carried out using the rotating-single-crystal method. The following data was established:-

1. The crystal system is orthorhombic.
2. Unit cell dimensions are a = 17.1Å, b = 10.2Å, C = 7.9_4Å; the volume of the unit cell = 1385Å^3.
3. There are 4 molecules of $Ø_3B$ per unit cell (based on a measured crystal density of 1.15g.cm^{-1}).
4. The space group is Pb Cn (D_{2h}^{14}, nO 60)

The normal number of equivalent general positions for this space group is 8. As there are only 4 molecules in the unit cell they must occupy special positions and conform to the symmetry of the special position. Of the three possible special positions for this space group, two require a centre of symmetry (which triphenylboron does not have) and thus are not applicable. The third requires a two-fold rotation axis, which this molecule can exhibit. This would mean that:-

a) There is a planar co-ordination around the boron atom.

b) Two phenyl rings (A and B) in triphenylboron are similarly inclined to the trigonal plane, with ring C at a different angle.

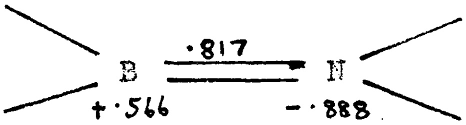


This confirms Ramsey's(115) interpretation of the ultraviolet spectra of triphenylboron. (Although, strictly speaking, Ramsey's study was carried out with triphenylboron in methylcyclohexane solution; $\emptyset_3B$ was thus in the liquid rather than the crystalline state).

To determine the angle of inclination of the phenyl rings to the BC_3 plane would require an intensity analysis of the diffraction pattern. This is made extremly difficult by the absence of a heavy atom in triphenylboron and the investigation was not pursued any further. The angles could, however, be estimated from a model of the unit cell.

The polarity of the boron-phenyl bond

In agreement with the majority of experimental evidence it has been established in this section that the boron-phenyl bond contains a good deal of π character. However, it still remains to explain the experimental evidence which leads to the opposite conclusions, i.e. Abel's'(27) work on the factors influencing the co-ordination of amines to boron attached to oxygen, and Dewar's(30) observation of the downfield shift in phenylboronic acid relative to boric acid. Both of these experimental observations indicate a loss of electron density from the boron atom when OR in $B(OR)_3$ (where R = H, alkyl) is replaced by a phenyl group. The amine complexing experiments indicate that this effect is most unlikely to be merely due to differences in effectiveness of back co-ordination to boron by phenyl or oxygen. Perhaps this 'anomalous' experimental evidence may be rationalised from theoretical considerations. Hoffmann(117) has carried out an electron population analysis on borazine, aminoborane and borazane type structures, using a molecular orbital method. In each of these three cases the nitrogen atom was found to be more negative than the boron atom. In the π system of the aminoborane structure (XVII), 0.23 of electronic charge is transferred from N to B, but the effect in the σ system is reversed (because of the electronegativity of the nitrogen atom), and the total charge transfer is



XVII

0.28 electron from B to N. It is probable that the high electronegativity of the phenyl group has a similar effect to that of the nitrogen atom, producing a net decrease of electron density on the boron atom. Thus, although it is true that the charge transfer is from phenyl to boron in the π system, the total charge distribution is in the opposite direction. Bond energies ~~and likewise dipole moment measurements~~ would be unaffected by this interpretation.

Section 3. The Thermochemistry of 2-chlorobenzo-2-bora 1, 3 dioxarole and related compounds

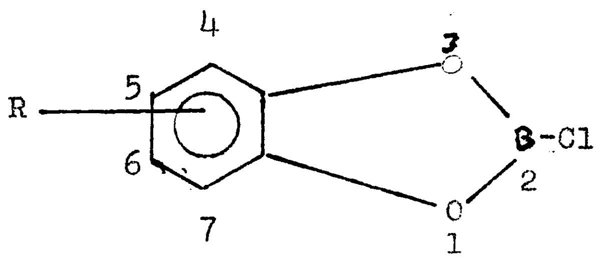
Purpose of Investigation

To synthesize the substituted 2-chlorobenzo-2-bora 1, 3 dioxarole derivatives and estimate the conjugative effect of the aromatic nucleus on the adjacent dioxaboron ring.

Nomenclature

These compounds are named using the nomenclature suggested by Dewar;$^{(1)}$since, however, this systematic nomenclature is somewhat lengthy, the 2-chlorobenzo-2-bora 1, 3 dioxarole nucleus will be denoted by the numeral XVIII. The substituted derivatives will be denoted by the same numeral followed by the substituent.

e.g.

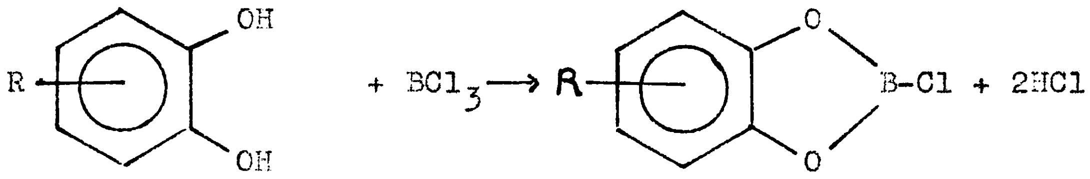


= XVIII (R = X)

The following compounds were prepared XVIII R = H, 5-Me, 5-Cl, 5-NO_2 and 4-MeO. (3-methoxy catechol was the only commercially available methoxy substituted catechol.

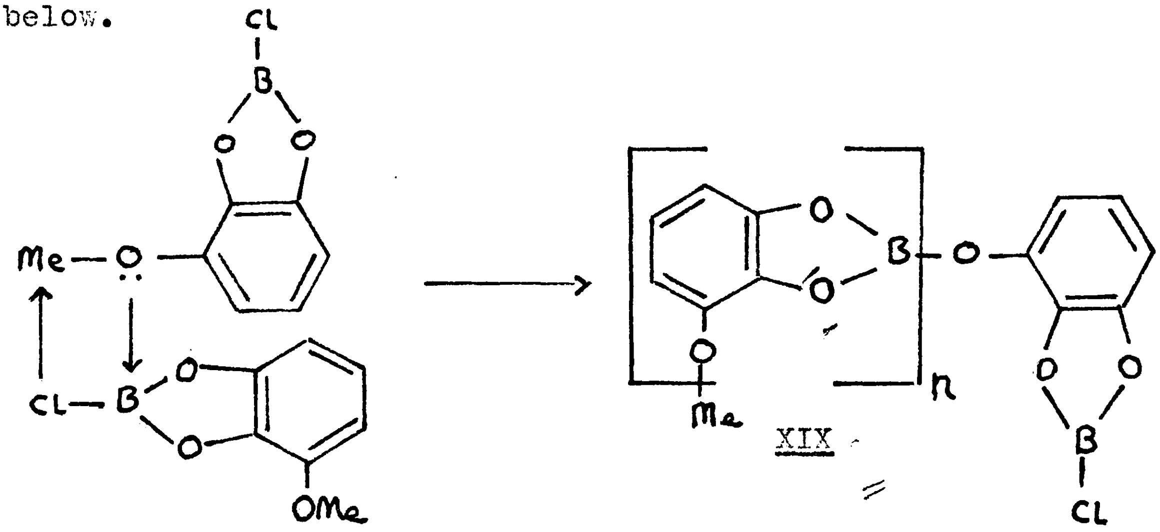
Method of Preparation

All the XVIII derivatives were readily prepared by adding the appropriate catechol, in suspension in methylene chloride, to a solution of boron trichloride in methylene chloride at -80°C, according to Gerrard's procedure.(51) After removal of the solvent, the product was purified by vacuum distillation; (except for XVIII (R = 5-NO_2) which exploded on distillation and was purified by crystallisation). All the products were stable crystalline solids and good yields were obtained. However, in the case of XVIII (R = 4-MeO), only a small yield of pure product was recorded (20%), together with a dark polymeric material which failed to distil. The polymer contained no hydrolysable chlorine, but reacted slowly with water to give boric acid and an aromatic hydroxy compound. The 4-methoxy derivative was slightly less thermally stable than the other substituted compounds (with the exception of XVIII R = 5-NO_2) and it could be slowly pyrolysed, (by pumping for 4 hours at 150°C/100 mm Hg), to give a similar polymer to that obtained in the preparation. A liquid collected in the cold



trap protecting the pump was tentatively identified as methyl chloride containing traces of boron trichloride. It is possible that the liquid identified as methyl chloride could have been 'trapped' methylene chloride solvent. Consequently the preparation of XVIII (R = 4-MeO) was repeated using carbon disulphide as solvent. A much improved yield was obtained (70%) and a very small amount of polymer. The pure compound XVIII (R = 4-MeO) was pyrolysed, as before, to give a polymeric product, and the liquid collected in the trap was positively identified as methyl chloride by comparison of its infrared spectrum with that of an authentic sample of methyl chloride. (See Fig. III)

A possible mode of elimination of methyl chloride during pyrolysis could involve the 4-centre mechanism illustrated below.



XIX

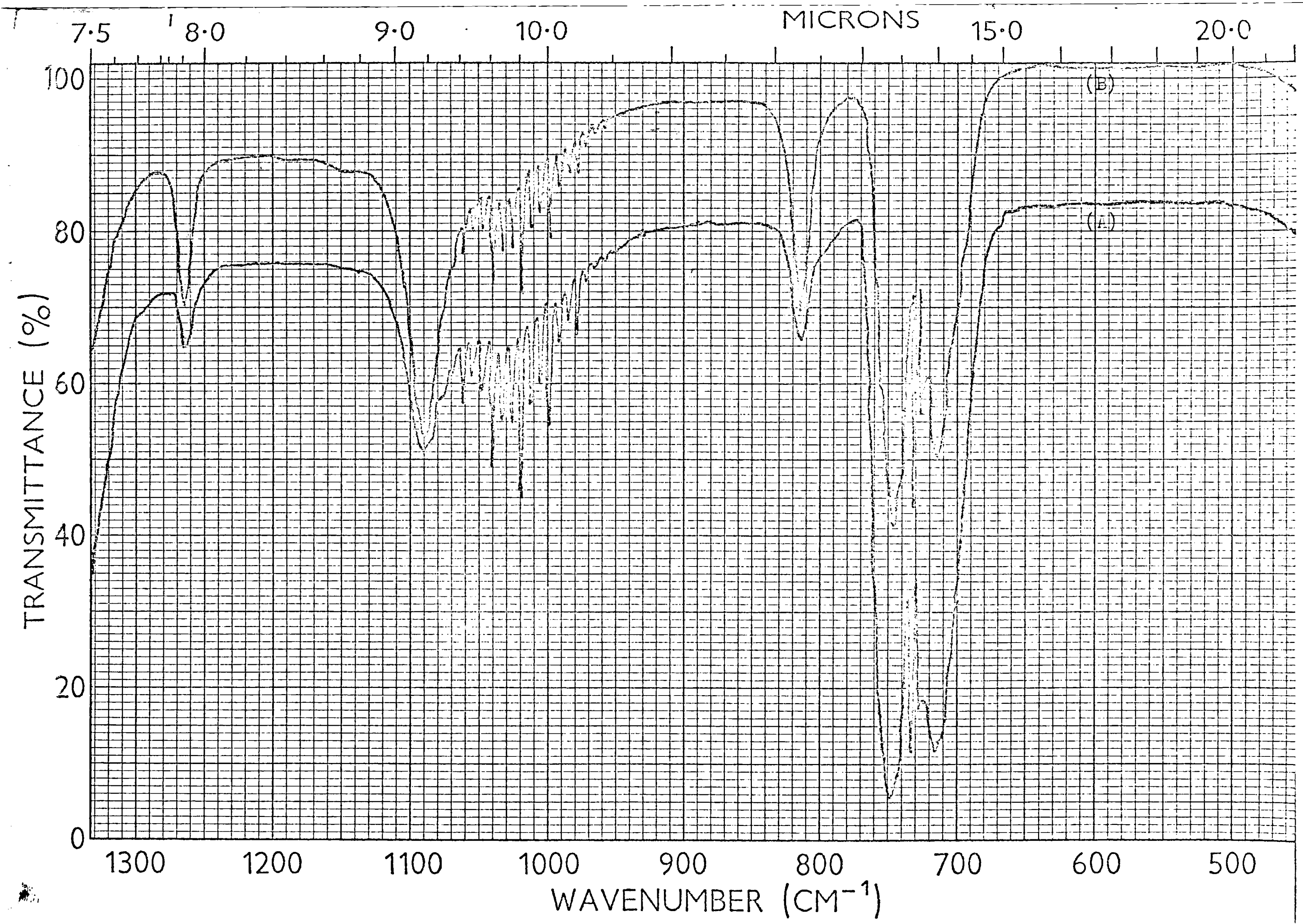
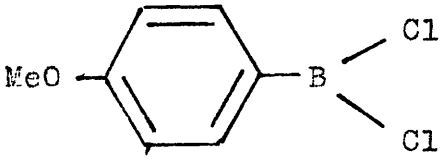


FIG.III. SPECTRUM(A)-METHYL CHLORIDE; SPECTRUM(B)-GAS SAMPLE FROM PYROLYTIC DECOMPOSITION OF XVIII(R = 4-MeO).

The polymeric residue had a boron content of 5.94% and compound XIX would require B = 8.0 %, hence it seems likely that the polymeric residue contains only a small amount of XIX. The above observation on the behaviour of this type of boron compound is by no means unique. Dandegoanker et al(118) have shown that when p-methoxyphenylboron dichloride (XX) was heated, methyl chloride was quantitatively evolved and a resin-like solid remained. On hydrolysis the resin yielded p-hydroxyphenylboronic acid.



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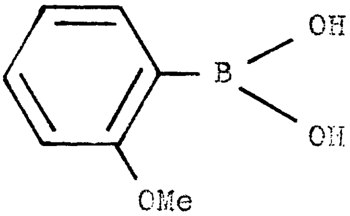
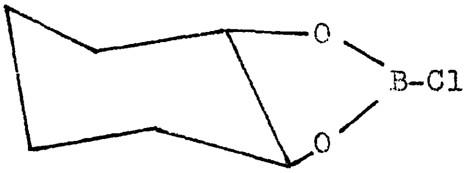


XXI

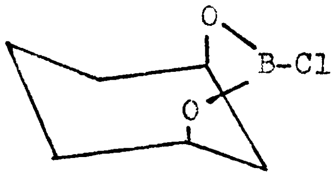
Eggers and Kettle(119) have recently found that ortho anisylboronic acid (XXI) sets to a hard resin when heated to 40 - 50°C under vacuum, and dehydration is accompanied by methanol elimination.

In deriving the conjugation energies in these compounds, it was considered necessary to have a reference compound which possessed a similar structure to the benzodioxarole system and was itself not capable of resonance. A suitable compound would have been 2-chloro 1, 3, 2 hexahydro-benzodioxaborolan (XXII), however an attempt to synthesize this compound by condensing cis 1, 2 cyclohexane diol with boron trichloride was unsuccessful.

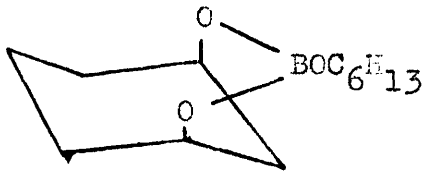


XXII

It has been mentioned in the introduction that the borolan system was strained and that it tended to relieve this strain by inter-molecular association. Such association is impossible in the case of XXII because of the puckered cyclohexane ring. Thus, for this reason, the molecule XXII is probably too unstable to be isolated. (If this molecule had been stable it would have been possible to estimate the inherent strain energy). In contrast to the five-membered boron heterocycles, the 1, 3 dioxaborinan ring is much less strained, and a stable bicyclic molecule containing a dioxaborinan ring fused to a cyclohexane ring was considered to be an equally suitable reference compound, e.g. 2-chloro 1, 3, 2 hexahydrobenzodioxaborinan (XXIII). Although this compound is unknown, the 2-hexoxy ester (XXIV) has been prepared by Dale (120), who realised that a trigonal boron atom could span the hydroxy groups in cis 1, 3 cyclohexane diol with little

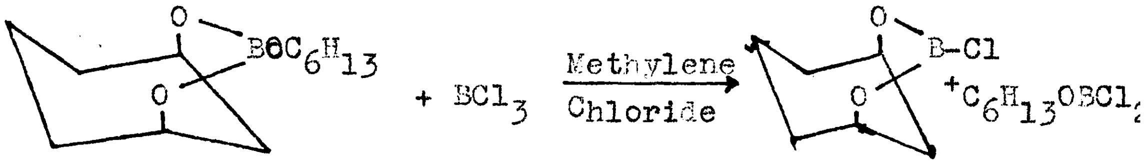


XXIII



XXIV

strain, and used it as a method of separating the cis and trans isomers of this compound. Compound XXIV was simply prepared by heating trihexylborate with cyclohexane 1, 3 diol (cis and trans mixture). The cis isomer forms XXIV and is distilled off (a colourless liquid), whilst the trans isomer forms a polymeric borate and remains in the reaction flask. To obtain XXIII the redistribution reaction:-



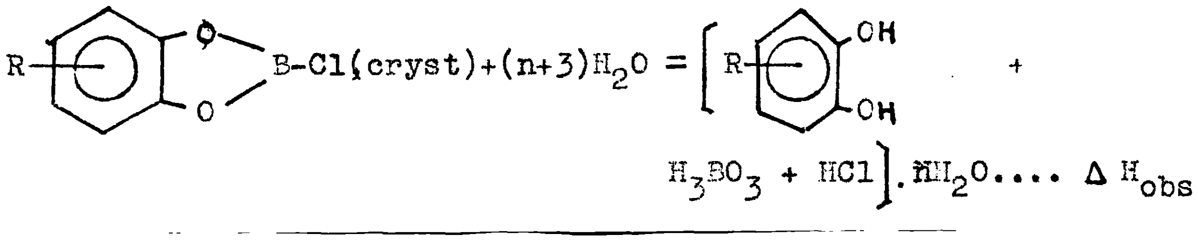
was applied. A similar redistribution reaction has already been demonstrated for the 2-butoxy esters of benzo-2-bora, 1, 3 dioxarole(121) and 1, 3 dioxaborolan.(122) The above reaction was, however, a failure and no identifiable products could be isolated. These results are in accord with the observations of Finch et al,(123) who studied the factors influencing the stability of 2-chloro and 2-alkoxy 1, 3 dioxaborinan compounds. The thermal stability of the

2-chloro derivatives decreased sharply upon substitution of the ring hydrogen atoms by methyl groups, whereas the stability of the 2-alkoxy esters increased. If XXIII and XXIV can be regarded as highly substituted 1, 3 dioxaborinans, then the instability of the 2-chloro derivative (XVIII) is rationalised.

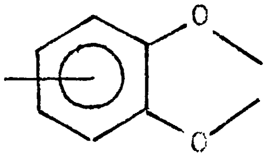
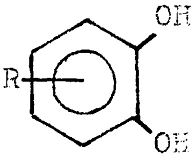
The reason why compounds containing the B-Cl link are preferred in solution calorimetry is because they hydrolyse rapidly and quantitively. Ester hydrolysis is an equilibrium process and it is difficult to know the position of equilibrium. However, the ester XXIV was shown to be a suitable compound for calorimetric study, since the half life of its hydrolysis in 0.1M sodium hydroxide was found to be 15 sec/25°, indicating that the reaction went quickly to completion.

Calorimetry

In excess water, the benzodioxarole derivatives are quantitively hydrolysed to boric acid, hydrogen chloride and the starting dihydroxy compound (although insufficient water leads to the preferential destruction of the boron-halogen bond). The thermochemical equation for the hydrolysis is:-

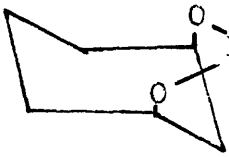
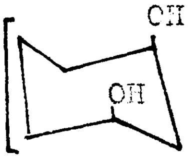


and hence

ΔH_f^o (R–  B-Cl, cryst) = ΔH_f^o (R–  , aq)

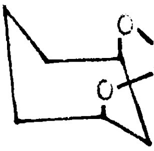
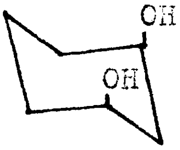
+ $\Delta H_f^o(H_3BO_3, aq)$ + $\Delta H_f^o(HCl\cdot\frac{n}{3}H_2O)$ - 3 $\Delta H_f^o(H_2O, liq)$ - ΔH_{obs}

The 2-hexoxy ester XXIV was hydrolysed in 0.1 M sodium hydroxide saturated with cyclohexanol, so that the cyclohexanol produced in the reaction can be assumed to form in its standard state.

 BOC_6H_{13} (liq) + $(n + 3)H_2O$ [ + H_3BO_3]. nH_2O

+ $C_6H_{13}OH$, liq...... H_{obs}

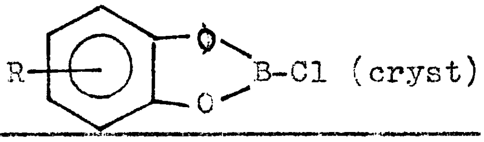
thus

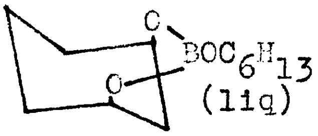
ΔH_f^o  BOC_6H_{13}, liq = ΔH_f^o  , aq + $\Delta H_f^o(C_6H_{13}OH, liq)$

+ $\Delta H_f^o(H_3BO_3, aq)$ - 3 $\Delta H_f^o(H_2O, liq)$ - ΔH_{obs}

The observed enthalpy changes for these hydrolysis reactions are collected in Table XXII.

TABLE XXII

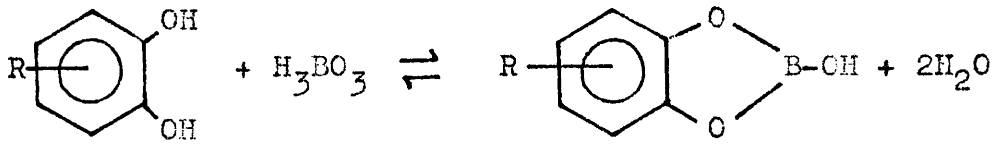
Enthalpies of hydrolysis of  (cryst)

R	N	ΔH_{obs} 25°(K.cal.mole^{-1})
H	2190	-22.7 ± 0.2
5-Cl	1520	-23.7 ± 0.15
5-Me(liq)*	1590	-26.65 ± 0.15
4-MeO	2050	-22.6 ± 0.25
5-NO_2	2370	-23.5 ± 0.15
	1740	-14.8 ± 0.2

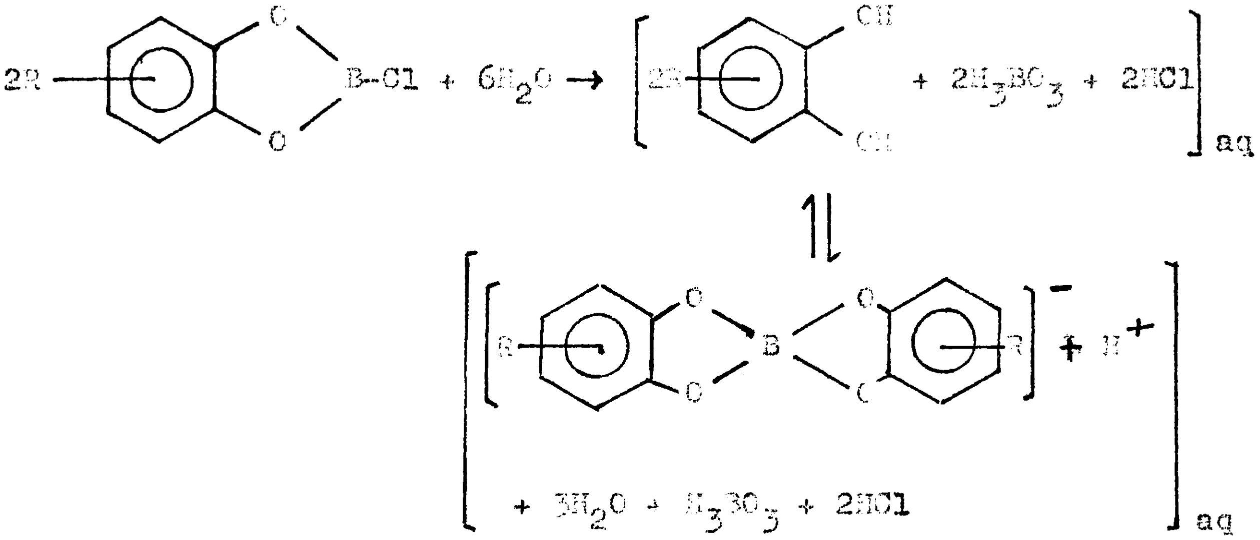
* at 25°C XVIII (R = 5-Me) is in the liquid state

In all of the above hydrolyses, the products include a diol and boric acid. It is possible that complexing reactions of the types (i) and (ii) may occur and lead to anomalous values of ΔH_{obs}

(i)



(ii)



The possibility of (i) and (ii) occurring was checked by determining the heat of solution of boric acid in (a) equimolar quantities of diol and hydrochloric acid (b) 2 x molar quantities of diol and hydrochloric acid, for every dihydroxy compound used in this investigation. The results (experimental section 5) showed that spurious thermal effects due to these equilibria were negligible.

Ancillary Data

The standard heats of formation of the benzodioxaroles molecules (XVIII) may be calculated with a knowledge of the enthalpies of formation of the substituted catechols. However, none of these values (with the exception of catechol) have been determined, consequently they were estimated using the Cox(62) bond energy scheme. As a check, the scheme was also applied to calculate the heat of formation of catechol and the value obtained (-87.4 K.cal.mole^{-1}) is in good agreement with an experimental value.$^{(124)}$ (ΔH_f^o catechol (g) = -86.6 K.cal.mole^{-1}). The enthalpies of vaporisation and fusion of the substituted catechols are also required, since the bond energy scheme gives only their gas phase heats of formation. These were estimated from the following relationships:

$$\Delta H^{298}_{vap}\ \text{substituted catechol (R=X)} = \frac{\Delta H^{298}_{vap}\ \text{XVIII (R=X)}}{\Delta H^{298}_{vap}\ \text{XVIII (R=H)}} \times \Delta H^{298}_{vap}\ \text{Catechol}$$

$$\Delta H_{fus}\ \text{substituted catechol (R=X)} = \frac{\Delta H_{fus}\ \text{XVIII (R=X)}}{\Delta H_{fus}\ \text{XVIII (R=H)}} \times \Delta H_{fus}\ \text{Catechol}$$

The heats of vaporisation and fusion of catechol were taken from ref. 124 and the rest of the terms, on the right-hand side of the above equation, were measured.

TABLE XXIII

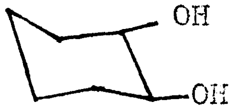
Enthalpies of fusion, vaporisation and formation of the substituted catechols

R	ΔH_{fus}	ΔH^{298}_{vap}	ΔH_f^o(g)	ΔH_f^o(cryst)
H	5.4	16.1	-65.1	-86.6
4-Me	5.4	16.6	-73.8	-95.8
4-Cl	6.3	16.2	-72.9	-95.4
4-NO_2	7.1	18.2	-69.0	-94.3
3-MeO	4.9	17.6	-102.9	-125.4

The data are in K.cal.mole^{-1} at 25°. An error of ±2 K.cal.mole^{-1} was assigned to all heats of formation. The enthalpies of solution in water of all the diols were measured and these are reported in Table XXIV.

TABLE XXIV

Enthalpies of solution of the substituted catechols (cryst) in water

R	N	ΔH_{obs}(K.cal.mole^{-1})
H	800	3.65 ± 0.05
4-Cl	660	4.20 ± 0.1
4-Me	850	3.65 ± 0.1
4-NO_2	1080	4.76 ± 0.01
3-MeO	3600	3.28 ± 0.01
	730	0.91 ± 0.04

In this and future tables N is the mole ratio of solvent to compound.

The standard heat of formation of cis cyclohexane 1, 3 diol is not known, but it was assumed to be the same as for cis cyclohexane 1, 2 diol (= -131.7 K.cal.mole^{-1})(125) A similar assumption was made regarding the heat of solution of cyclohexane 1, 3 diol in water. The heat of formation of hexanol, liq (= -91.75 ± 0.5 K.cal.mole^{-1}) was obtained from ref. 125 and the rest of the ancillary data used in calculations was taken from Table XV.

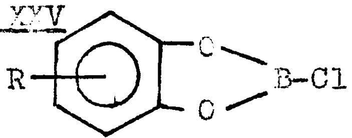
Enthalpies of transition

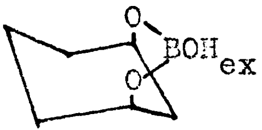
As in the previous two sections, enthalpies of transition (liq to gas) were determined using the Cartesian manostat method. The experimental data are represented in the form

$$\log_{10}P(\mathrm{mm}) = a - \frac{b}{T^{o}A}$$

a and b were obtained from a least squares analysis. The results are summarised in Table XXV.

TABLE XXV

Latent heats of vaporisation of 

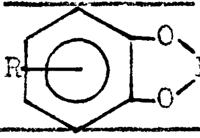
R	range °C	a	$10^{-3}b(^{o}K)$	ΔH_{vap}^{T}	ΔH_{vap}^{298}
H	72-120	8.96	2.68	12.3	13.2
5-Cl	75-150	8.40	2.68	12.3	13.3
5-Me	63-130	8.83	2.77	12.7	13.6
4-MeO	85-125	8.73	2.92	13.4	14.5
5-NO_2	-	-	-	-	14.9*
	126-187	9.37	3.55	16.3	18.9

* estimated from a plot of molecular weight vs ΔH_{vap}^{298}.

All the enthalpies of transition are in K.cal.mole^{-1} with an error of ± 0.2 K.cal.mole^{-1}. (An error of ± 1 K.cal.mole^{-1} was assigned to XVIII (R = 5-NO_2).

Enthalpies of fusion of the crystalline benzodioxarole derivative were obtained by measuring their heats of solution in an inert solvent (benzene).

TABLE XXVI

Enthalpies of solution of R  B-Cl(cryst) in benzene

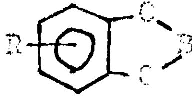
R	N	ΔH_{obs} 25°(K.cal.mole^{-1})
H	175	4.31 ± 0.01
5-Me	170	4.1 ± 0.1 (20°C)
5-NO_2	290	$4.6_5 \pm 0.1$
5-Cl	-	4.5 ± 0.2*
4-MeO	200	4.7 ± 0.1

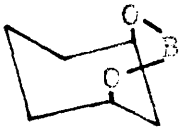
*estimated value. Lack of compound precluded the determination of ΔH_{fus}.

The solution of XVIII (R = 5-Me) was carried at 20° because the compound melts at 21°.

Combination of the data from Tables XXII to XXVI yields the heats of formation of the substituted benzodioxarole derivatives, in the crystalline, liquid and gaseous states.

TABLE XXVII

Heats of formation of R-B-Cl(cryst, liq and gas)

R	ΔH_f^o(cryst)	ΔH_f^o(liq)	ΔH_f^o(g)
H	-151.5	-147.2	-134.0
5-Me	-160.8	-156.7	-143.1
5-Cl	-158.7	-154.7	-141.4
5-NO_2	-157.2	-152.6	-137.7 ± 2.2
4-MeO	-190.7	-186.0	-171.5
BOHex	-	-259.0 ± 1.6	-240.2 ± 1.6

values are in K.cal.mole^{-1} with an error of ± 2.0 K.cal.mole^{-1} except where otherwise indicated.

Conjugation energies

The conjugation energies of the benzodioxaborole derivatives were evaluated by comparing the experimental gas phase heats of formation with the heats of formation calculated for a non-resonant reference structure (i.e. one of the resonance structures), using a standard set of bond energies and the equation:

$$-\Delta H_f^o(g) = \Sigma E - \Sigma \Delta H_f^o \text{ (atoms)}$$

$\Sigma \Delta H_f^o$ (atoms) = sum of the enthalpies of atomisation of the constituent elements from their standard states at 25^o

ΣE = bond energies (25^o) summed over the whole molecule

$\Delta H_f^o(g)$ = gas phase enthalpy of formation of the molecule at 25^o.

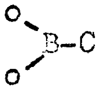
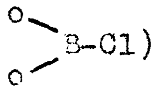
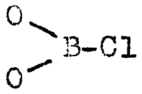
The bond energies were taken from Cox(62) but this author does not list either boron-oxygen or boron-chlorine bond energies. Since all the benzodioxaborole molecules contain the group , E(B-Cl) and E(B-C) were evaluated in the form of the group bond energy E(), by applying the same bond energy scheme to diethylchloroboronate ($EtO)_2BCl$; this molecule has been studied thermochemically.(18) The group bond energy $E(C_{b3} - NO_2)$ was calculated from the Cox scheme and the known standard heat of formation of nitrobenzene. This derived datum was checked by using it to calculated the standard heat of formation of p-nitroaniline. A value (17.5 K.cal.mole^{-1}) for ΔH_f^o p-nitroaniline (g) was obtained, in excellent agreement with the experimental value (17.4 K.cal.mole^{-1})(124) All the bond energies and enthalpies of atomisation employed in calculations are now summarised in Tables XXVIII and XXIX.

TABLE XXVIII

Bond and Group Energies (taken mainly from Cox(62))

Bond or Group	Energy (K.cal.)	Bond or Group	Energy (K.cal)
C_6H_4	1114.5	$(C_{sp3} - H)^{111}$	98.3
C_6H_3	1012.7	$C_{b_3} - Cl$	85.7
	357.0	$C_{b_3} - OH$	204.2
B - O	124.4	$(C_{sp3} - H)^{111}_{o}$	95.7
$C_{sp3} - C_{sp3}$	85.0	$C_{sp3} - O$	91.75
$C_{b_3} - O$	94.6	$(C_{sp3} - H)^{11}_{o}$	95.3
$C_{b_3} - NO_2$	248.8	$(C_{sp3} - H)^{1}_{o}$	94.4
$C_{sp3} - C_{sp2}$	89.9	$(C_{sp3} - H)^{11}$	97.5

Bonds written $C_{b_3} - X$ indicate that the carbon atom is part of an aromatic ring. The primes used in connection with C_{sp3} - H bonds, distinguish between primary, secondary and tertiary C - H bonds, e.g. $(C_{sp3} - H)^{111}$ represents a carbon atom substituted by three hydrogen atoms. Carbon-hydrogen bonds which are adjacent to an oxygen atom are indicated with a subscript O.

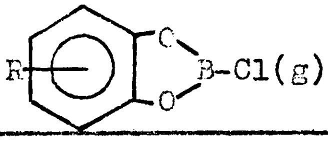
TABLE XXIX

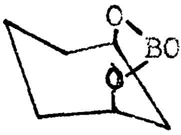
Enthalpies of formation of the gaseous atoms$^{(62)}$

Species	$\Delta H_f^o(g)$ K.cal.mole^{-1}
C (graphite)	170.9
H (g)	52.09
Cl (g)	28.94
O (g)	59.54
N (g)	112.9
B (cryst)	132.8 ± 4$^{(10)}$

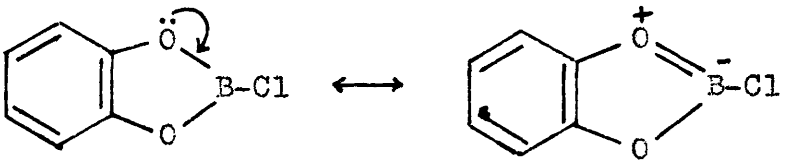
In Table XXX, the experimental gas phase heats of formation of the benzodioxarole derivatives are compared with those calculated from the above data.

TABLE XXX

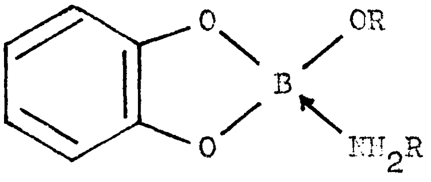
Experimental and calculated heats of formation of 

R	$\Delta H_f^o(g)$ expt.	$\Delta H_f^o(g)$ calc.	$\Delta H_f^o(g)$ expt. - $\Delta H_f^o(g)$ calc.
H	-134.0	-146.9	12.9 ± 4.0
5-Me	-143.1	-154.8	11.7 ± 4.0
5-Cl	-141.4	-154.0	12.6 ± 4.0
5-NO_2	-137.7	-150.0	12.3 ± 4.1
4-MeO	-171.5	-184.0	12.5 ± 4.0
 BOH$_{ex}$	-240.2	-257.5	17.3 ± 4.3

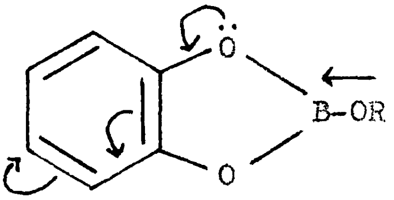
A striking feature of the above data is that the difference between experimental and calculated heats of formation for the XVIII derivatives is positive, indicating that these molecules are strained overall. If the benzodioxarole system can be considered as formed from the fusion of a benzene ring with a 'highly strained' dioxaborolan ring, then the figure ~ 12 K.cal.mole^{-1} may be interpreted as the resultant of two opposing effects. (i) strain due to the dioxaborolan ring, (ii) resonance stabilisation contributed by structures of the type:



In this case the stabilisation energy only partially offsets the strain energy. The fact that the hexahydrobenzodioxaborinan derivative (XXIV) possesses a greater strain (~ 17 K.cal.mole^{-1}) indicates that this interpretation is justified. (A trigonal boron atom is more easily incorporated into a six-membered than into a five-membered ring). The strain in the 2-hexoxy ester (XXIV) compares well with that in 2-chloro 1, 3 dioxaborinan (~ 13 K.cal. mole^{-1}) and the small difference may be attributed to steric interactions of the substituents in the two cis-fused rings of the ester. It was mentioned in the introduction that benzodioxarole derivatives (XVIII), (in contrast to boroxarophenanthrene (XV) compounds), readily undergo hydrolysis and form stable 1 : 1 addition compounds with amines (XXV). The electron shift (XXVI) was postulated(53) to explain this behaviour.



XXV



XXVI

A better explanation, however, would be in terms of the relief of ring strain in the benzodioxarole nucleus, by conversion of the boron atom from trigonal to tetrahedral geometry, at the expense of resonance stabilisation.

The other interesting point which emerges from the data in Table XXX is that substituents in the benzene ring have little effect on the overall resonance energy of the molecule. The values given in the fourth column of Table XXX are not related to the electron directing properties of the substituents. However, the standard heats of hydrolysis of these molecules do show some slight correlation with the electron releasing or donating effects of the substituents (Table XXXI). The standard heat of hydrolysis (ΔH_h^o) is the enthalpy change on hydrolysis when all the products are referred to their standard states.

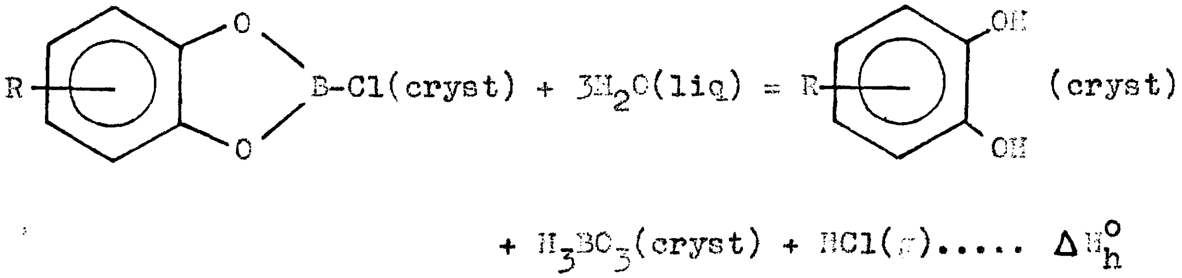
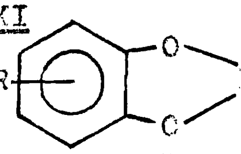
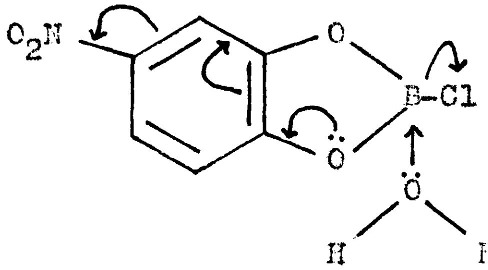


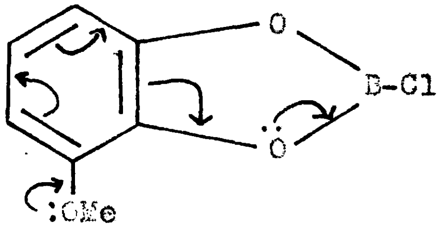
TABLE XXXI

Standard heats of hydrolysis of R-  B-Cl (cryst)

Substituent	ΔH°_h (K.cal.mole^{-1})
H	-13.7
5-Me	-13.5
4-MeO	-13.1
5-Cl	-15.2
5-NO$_2$	-15.6

The greater, i.e. the more negative, the standard heat of hydrolysis, the more readily hydrolysed is the compound.





π electron withdrawing (-R) substituents ($-NO_2$) will make the boron atom relatively more nucleophilic, thus promoting the co-ordination of water and the subsequent hydrolysis of the B-Cl bond. π electron releasing (+R) substuents (Cl, MeO, Me) will have the opposite effect, tending to stabilise the boron atom with respect to nucleophilic attack. (Only the chloro derivative has an anomalous standard heat of hydrolysis). However, the relative differences in ΔH_h^o are too small to have any significant effect on the experimental enthalpies of formation.

Estimation of strain and conjugation energies in the benzodioxarole system

The strain energy in the benzodioxarole system may be estimated by applying a simple geometric method based on bond lengths and bond angles. Three assumptions are made:

1) The strain is angular, i.e. due to distortion of the bonds from their valency angles.
2) Bond lengths are constant and transferable.
3) BOC and BCC angles are constant ($109\frac{1}{2}^o$).

The bond lengths were selected from 'Interatomic distances',(111) and are collected in Table XXXII.

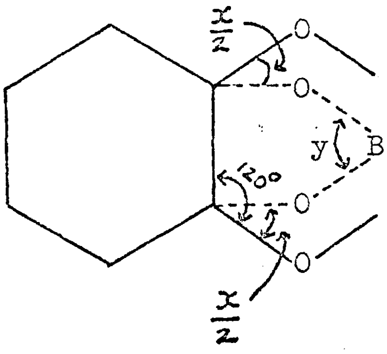
TABLE XXXII

Bond lengths used in strain calculations

Bond	Distance Å	Bond	Distance Å
B-S	1.85	$C_{sp}3$-O	1.43
B-O	1.39	$C_{sp}3$-S	1.81
B-N	1.42	C_{bz}-O	1.36
B-C_{bz}	1.52	C_{bz}-C_{bz}	1.39
C_{sp3}-C_{sp3}	1.54	C_{bz}-N	1.43

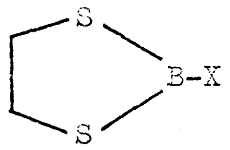
C_{bz}-X indicates that the carbon atom is part of an aromatic ring.

Consider the benzodioxarole nucleus

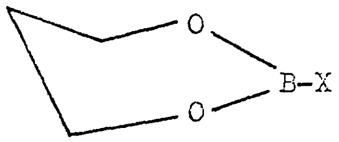


Strain energies are derived by considering the change in two parameters, (1) the base angle (120° in the case of benzodioxarole, (2) the angle y.

Method. The skeleton of the molecule is drawn to some suitable scale on the basis of known bond lengths and angles. In order that the ring may be formed (dotted line) the base angle has to change by an angle x, thus setting up strain in the molecule. When x is negative, the base angle decreases from its optimum value and when x is positive the base angle increases. When the ring has formed the angle OBO = y, and incorporation of a trigonal boron atom into the ring leads to a change in strain = $120^{\circ}-y = \theta^{\circ}$. The technique was applied to two rings (1,3 dithioborolan and 1,3 dioxaborinan) for which the strain is known(Table V).



$x = 2^{\circ}$, $\theta = -18^{\circ}$



$x = 3^{\circ}$, $\theta = 20^{\circ}$

The base angle in the case of the 1,3 dioxaborinan molecule was considered to be 90°, and a strain of 12.7 Kcal.mole^{-1} was attributed to this ring (although, from geometrical considerations, the heterocyclic ring of the 2-hexoxy ester (XXIV) has exactly the same dimensions as the dioxaborinan ring, the value (~ 17 Kcal.mole^{-1}) was not considered to be a measure of the strain in the six-membered ring for the reason already outlined). The strain in the dithioborolan ring was taken as the mean value for 2-chloro and 2-phenyl derivatives. (4.3 Kcal.mole^{-1}). Equations (i) and (ii) were solved simultaneously for x and θ, giving x = 3.6 Kcal.mole^{-1}. and θ = -0.3 Kcal.mole^{-1}.

$2x - 18\theta = 12.7$........ (i)

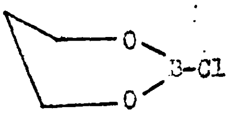
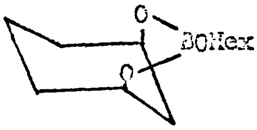
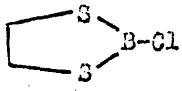
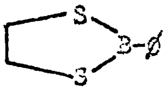
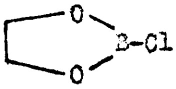
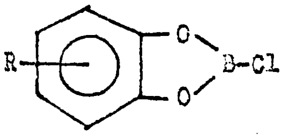
$3x + 20\theta = 4.3$......... (ii)

~~and θ = -0.3 K.cal.mole~~$^{-1}$.

Values of the strain energy calculated for benzodioxarole (XVIII) and 1, 3 dioxaborolan rings are given in Table XXXIII.

TABLE XXXIII

Strain energies in heterocyclic boron compounds

Compound	x°	y°	ϵ(120-y)	Strain (K.cal.mole^{-1})
	2°	138°	-18°	12.7 ± 5.2
	2°	138°	-18°	17.3 ± 4.3
	3°	100°	+20°	3.0 ± 4.3
	3°	100°	+20°	5.6 ± 4.7
	-9°	111°	+ 9°	~ 35
	-23°	106°	+14°	~ 86

The limits of uncertainty were obtained by combination of constituent error, which include $\Delta H_f^0(B,g) = \pm 4$ K.cal.mole^{-1}. Since the same sources were used for evaluation of ring strain, the differences are accurate to ±2.0 K.cal.mole^{-1}.

The estimated strain in 2-chloro 1, 3 dioxaborolan ($\sim$ 35 K.cal.mole^{-1}) is in keeping with the 'highly strained' nature of this compound. In the benzodioxarole system the strain is $\sim$ 86 K.cal.mole^{-1} and this leads to a total conjugation energy of $\sim$ 74 K.cal.mole^{-1}. Although this figure seems excessive it compares favourably with the conjugation energy in the unstrained borazole derivatives (this has been calculated from the gas phase heats of formation in Table VI, assuming bond transferability and using $\bar{D}$(N-B) $\sim$93, $\bar{D}$(B-C) = 105.3 and $\bar{D}$(B-H) $\sim$ 98 K.cal.mole^{-1}.

TABLE XXXIV

Conjugation energies of borazole and trichloroborazole

Compound	$\Delta H_f^o(g)$	Conjugation energy	Source
borazole	-197.0	146	40
"	-129.6	71	42
B-trichloroborazole	-256.1	66	40
"	-255.4	65	41

values are given in K.cal.mole^{-1}.

The considerable resonance energy in an unstrained hetereoaromatic boron compound is also reflected in its chemical properties. Thus 10, 9 boroxaro (XV) and 10, 9 borazarophenanthrene (XIV) (strain energies calculated by the geometric method are $\sim$ 3 and $\sim$ 5 K.cal.mole^{-1} respectively) are stable in strong alkaline solution and the latter compound is unaffected by both boiling concentrated acid and alkali.(56)(57)(The lower stability of the oxygen heterocycle compared with that of the nitrogen compound (XIV) reflects the relative abilities of these atoms to back-donate to the boron atom). In both these cases nucleophilic attack at the boron atom is unfavourable because conversion of boron from an sp^2 to an sp^3 hybridised state would destroy the aromaticity of the central ring.

A number of examples have been given in this thesis in which strained heterocyclic boron compounds, by changing from a trigonal to a tetrahedral configuration about the boron atom, relieve the strain. This was postulated as the reason why the benzodioxarole derivatives form stable adducts with amines. If, however, the geometric strain method is applied to benzodioxarole containing boron in both configurations, the total decrease in strain energy in going from sp^2 to sp^3 geometry is $\sim$ 3 K.cal.mole^{-1} ($\sim$ 70 K.cal. mole^{-1} conjugation energy is lost in this process). The geometric method in this respect is highly unsatisfactory because it makes the angle Y such an insensitive function of ring strain. It is possible that bond bending is an important factor in strained molecules and consequently it is wrong to assume a rigid σ skeleton.

Experimental

Section 1. Calorimetry

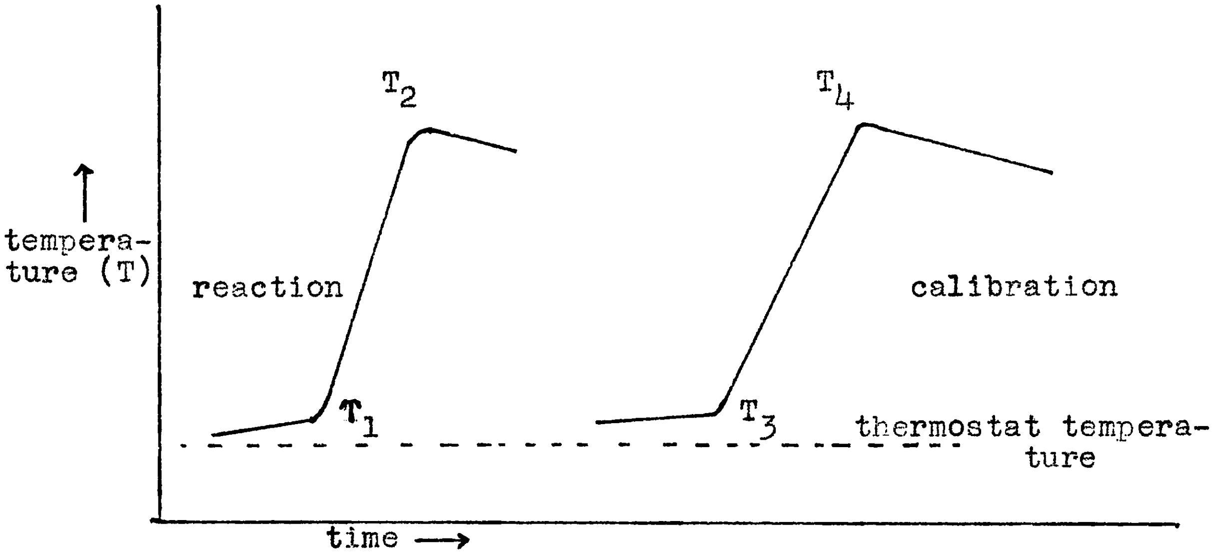
The principle of the calorimetric method is to measure the temperature change produced by a known weight of sample undergoing reaction or solution, and then to introduce a known amount of heat (measured electrically) and again determine the temperature rise; hence by proportion the heat change per unit mass of sample may be evaluated.

The Calorimeter

The calorimeter, based on a design already developed in this laboratory(90) was of the constant temperature environment ('isothermal') type. It consisted of a round-bottomed, flanged, glass Dewar vessel, approximately 2" internal diameter, and a flanged lid containing a number of ground glass sockets (see Figs. IV and V). The stirrer and the ampoule breaker were mounted in the sockets via precision-bore tubing. Additional holes carried the thermistor (sealed in a B10 leak), the heater and a platinum resistance thermometer. A remaining B.10 socket was used as a nitrogen gas inlet or outlet, and sometimes to carry a cooling tube. The sample was contained in a thin glass ampoule, blown on the end of a B.7 socket and affixed to the ampoule breaker via a B.7 cone. The heater was constructed from 'Constantin' wire (47 gauge, 50 /ft.) would spirally on a glass forma and soldered to leads made of copper wire (0.027" diameter). Thermal conduction was improved by submerging the coil in transformer oil, the whole being encased in a thin glass sheath. Temperature changes were measured with a thermistor (F.53, Standard Telephone & Cable Ltd.), which is a resistance with a high negative temperature coefficient. The resistance (Ω) and temperature (^{o}K) are connected by the expression:

$$R = A \exp. \frac{B}{T}$$

A and B are the thermistor constants (B is < 0). Consider the case of an <u>exothermic</u> reaction:



During the run, two changes in temperature are recorded; the reaction change ΔT^1 and the calibration change ΔT.

If $\Delta T^1 = T_2 - T_1$ and $\Delta T = T_4 - T_3$

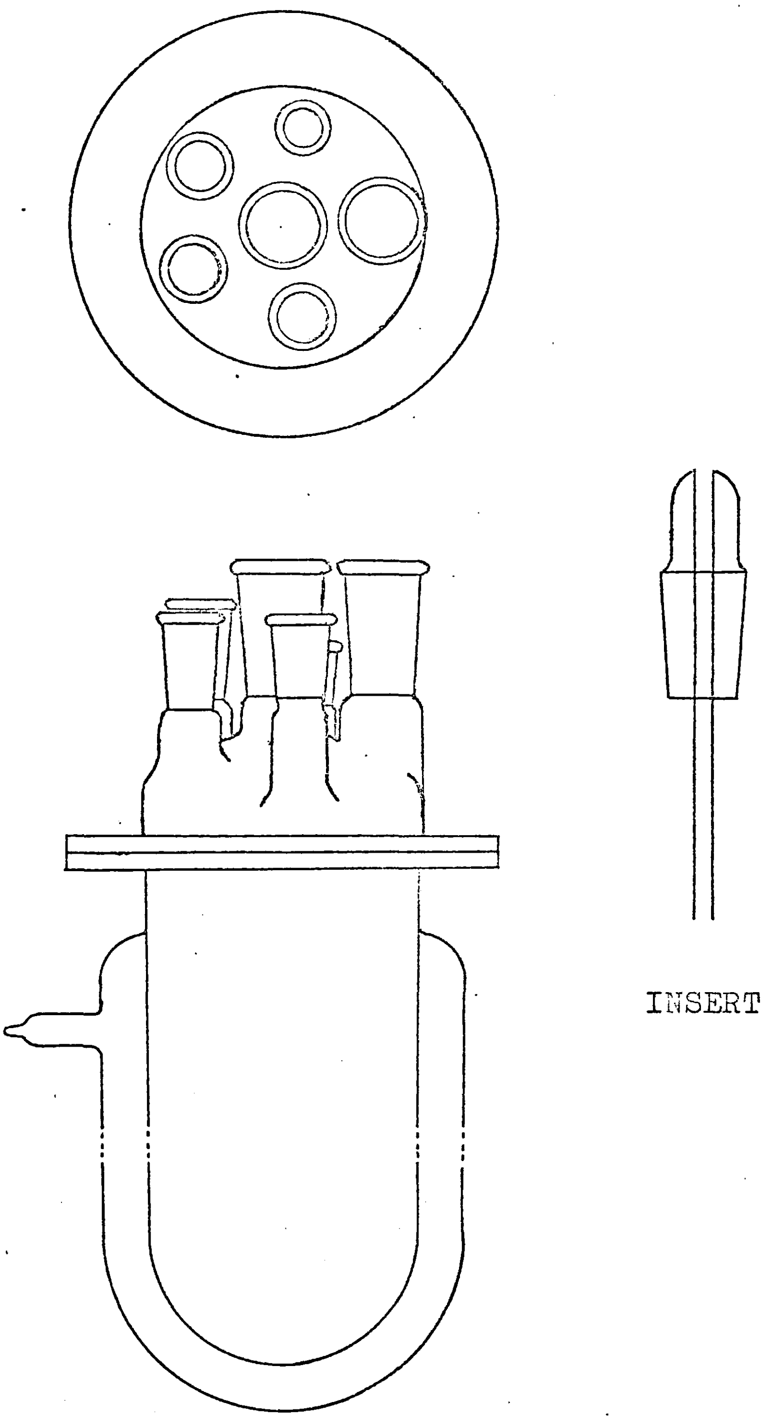
then $$\frac{\Delta T^1}{\Delta T} = \frac{\log \frac{R_1}{R_2} \cdot \log \frac{R_4}{A} \cdot \log \frac{R_3}{A}}{\log \frac{R_3}{R_4} \cdot \log \frac{R_1}{A} ; \log \frac{R_2}{A}}$$

If $T_1 \sim T_3$ and $T_2 \sim T_4$

then $$\frac{\Delta T^1}{\Delta T} \doteq \frac{\log R_1 - \log R_2}{\log R_3 - \log R_4}$$

However, it is preferable not to use this simple expression since often $T_1 \neq T_3$ and $T_2 \neq T_4$. To determine the temperature changes, the thermistor constants must be known. They were evaluated by calibrating the thermistor over the range 22 - 28°C against a Beckmann thermometer which had been pre-calibrated against a standard N.P.L. calibrated thermometer (± 0.005°C). The thermistor formed one arm of a Wheatstone network, with fixed ratio arms of 3 KΩ and a variable arm measuring from 0 to $10^4 \Omega$ (Decade resistance box). The out-of-balance bridge current was detected on a Scalamp galvonometer (7902/S W.G. Pye & Co.Ltd.). The electrical calibration circuit is shown in Fig. VI. The current was from a mains-powered constant potential (6 volts) D.C. source (Ether Ltd.). All the potential drops were measured with a Tinsley potentiometer (type 3387.B) used in conjunction with a Scalamp galvonometer of the above type; readings were accurate to

± 5 x 10^{-5} volts. The potentiometer standard cell was a Weston-Normal standard cell. (Cambridge Instrument Co.Ltd.). Calibration times were measured with an electric timer which was accurate to ± 0.005 sec. (Sangamo-Weston). Resistors for the potential divider circuit were supplied by Arcol Precision Resistors (2W, tolerance to 0.025%). The circuit standard resistance (guaranteed 0.9996 Ω) was obtained from Cambridge Instrument Co.Ltd. All resistances had a temperature coefficient better than 20 ppm per degree centigrade. Samples were weighed on a balance sensitive to ± 5 x 10^{-5}g. The whole calorimetric run was monitored with a miniature platinum resistance thermometer (100 Ω, Degussa) coupled to a six-inch potentiometric recorder (Elliott) accurate to ± 0.01°C.



INSERT

FIG.IV THE SOLUTION CALORIMETER.

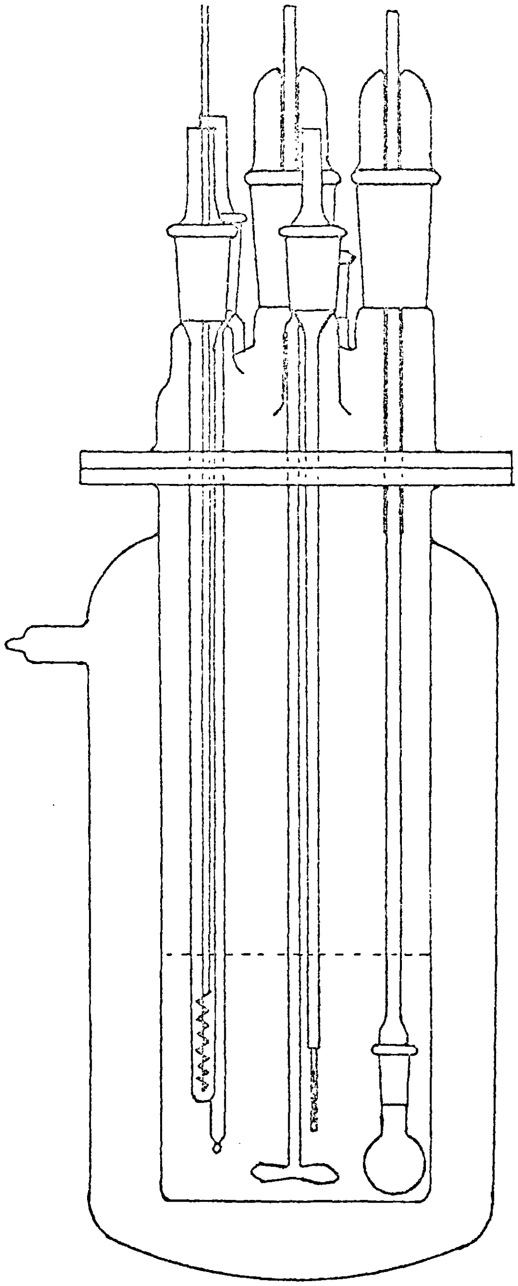


FIG.V THE SOLUTION CALORIMETER(LOADED).

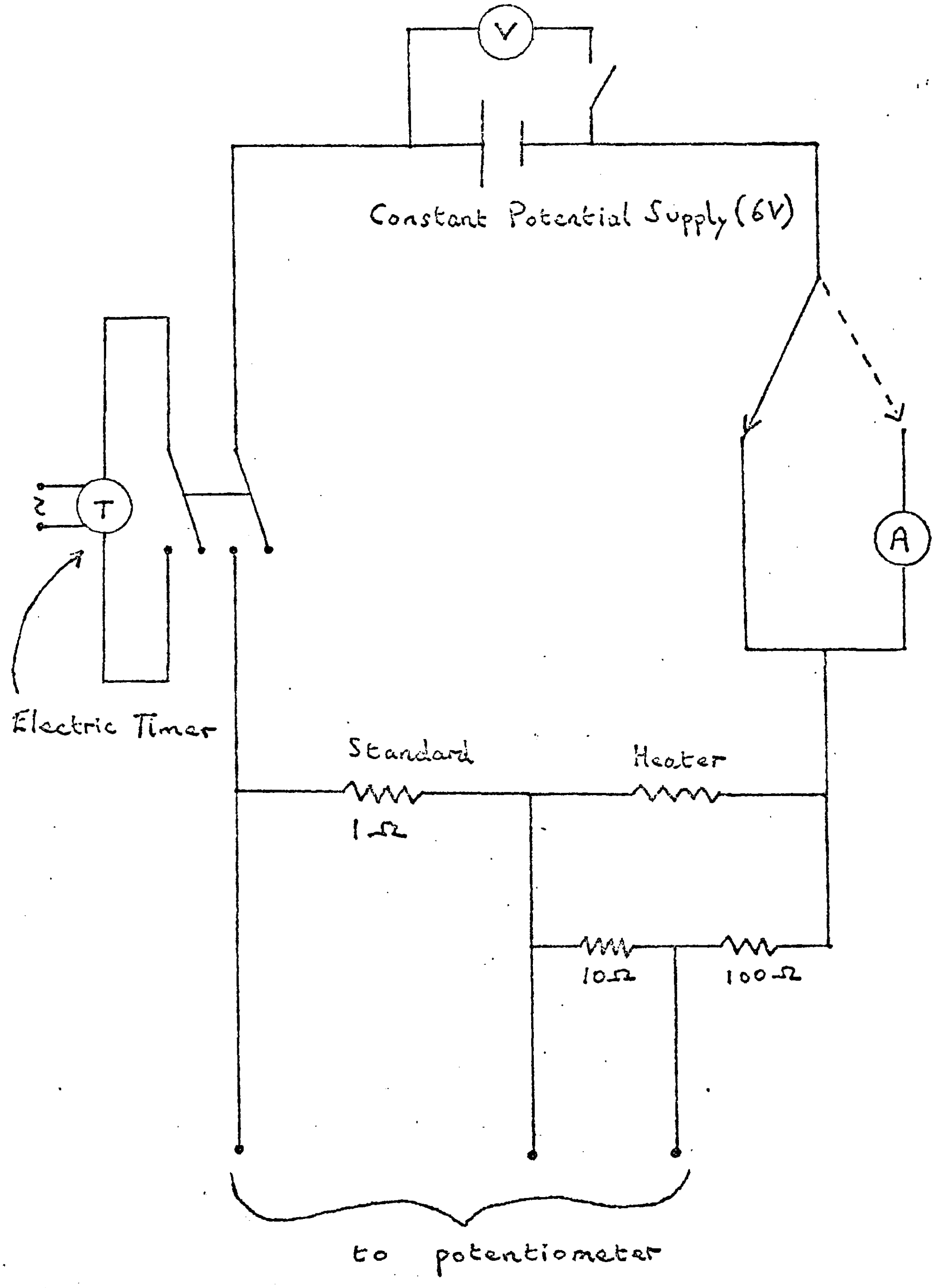


FIG VI HEATING CIRCUIT DIAGRAM

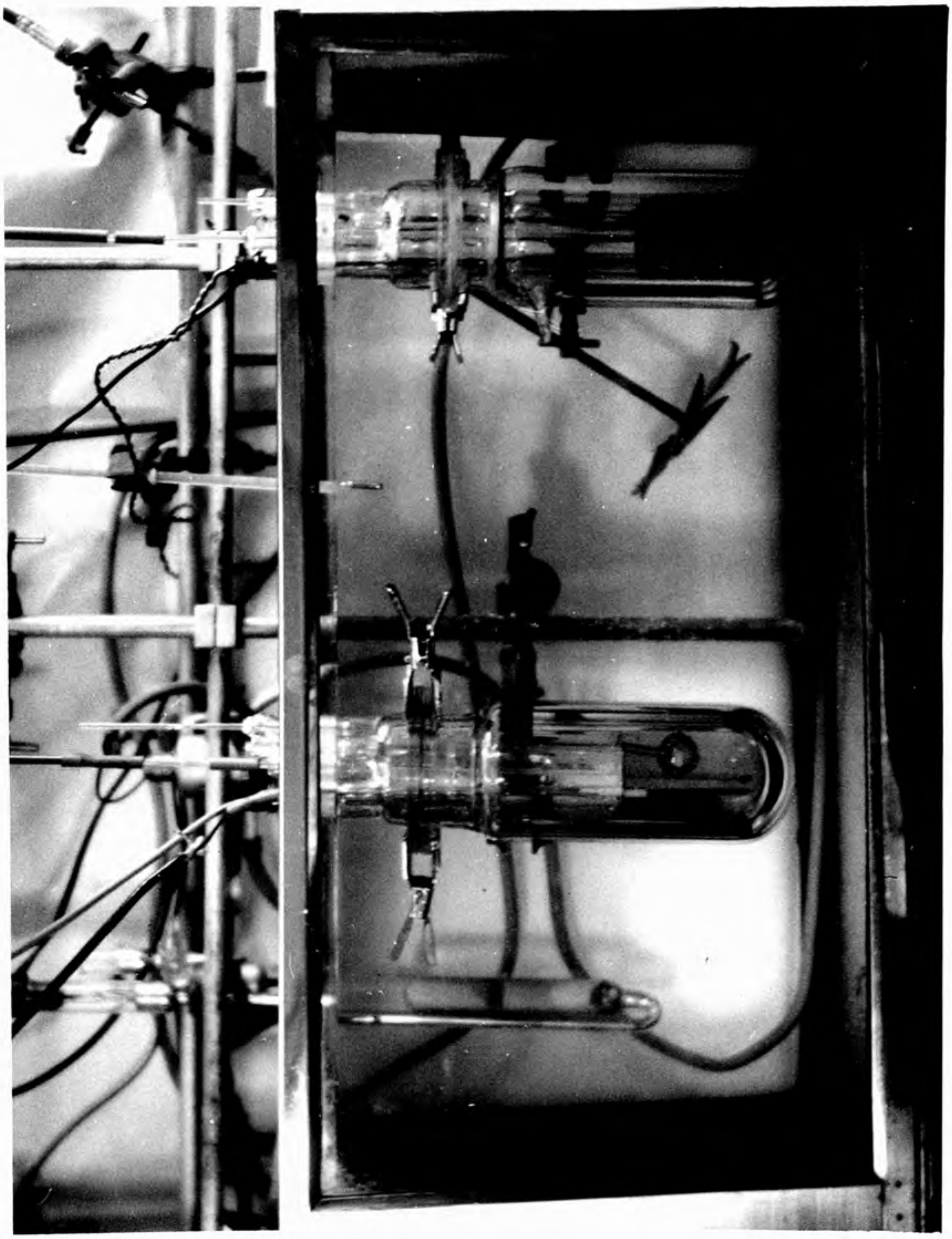
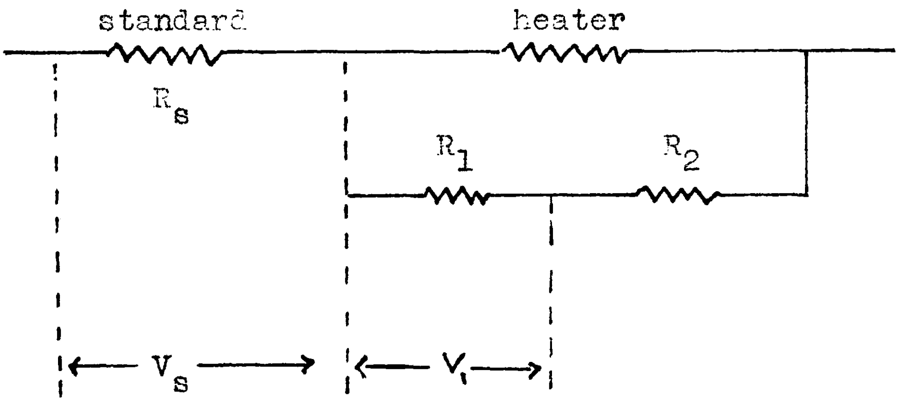


FIG. VII. THE CALORIMETERS IN OPERATION.

The heat change (Q) when a weight of compound (W) reacts is given by the expression:

$$Q = \frac{\text{electrical energy}}{J \times W} \times \frac{\Delta T\ \text{reaction}}{\Delta T\ \text{calibration}}\ \text{cal.gm}^{-1}$$

consider the following section of Fig. VI.



During the experiment two potential readings are recorded; that across the standard resistance(V_s) and that across the 10 Ω resistance (R_1) of the potential divider (V_1).

The power output (P) across the heater may be shown to be

$$P = V_1 \cdot \left[\frac{R_1 + R_2}{R_1}\right] \cdot \left[\frac{V_s}{R_s} - \frac{V_1}{R_1}\right] \quad \text{Watts}$$

since $R_1 = 10\,\Omega$ $R_2 = 100\,\Omega$ and $R_s = 1\,\Omega$

then $P = 11V_1 \left\{V_s - \frac{V_1}{10}\right\}$ Watts

$\therefore$ electrical energy $= 11V_1 \left\{V_s - \frac{V_1}{10}\right\} t$ Joules.

where t = cal-ibration time in seconds.

The complete expression for the enthalpy change is thus:

$$H = \frac{f.11V_1 \left\{V_s - \frac{V_1}{10}\right\} . M.t.\log\frac{R_1}{R_2} . \log\frac{R_3}{A} . \log\frac{R_4}{A}}{10^3 . J . W . \log\frac{R_4}{R_3} . \log\frac{R_1}{A} . \log\frac{R_2}{A}} \text{ K.cal.mole}^{-1}$$

f = factor correcting for the heater lead resistance (varies between 0.990 and 0.993).

V_1 = potential across 10 Ω resistance of the potential divider circuit (in volts).

V_s = potential across the standard resistance (in volts).

t = heating time (in seconds).

M = molecular weight.

A = thermistor constant (in Ω.)

R_1, R_2, R_3 and R_4 are resistances corresponding to temperatures T_1, T_2, T_3 and T_4 (°A).

W = weight of sample (in g.)

J = 4.1840 abs. joules (defined).

Thermal leakage correction

See fig. viii.

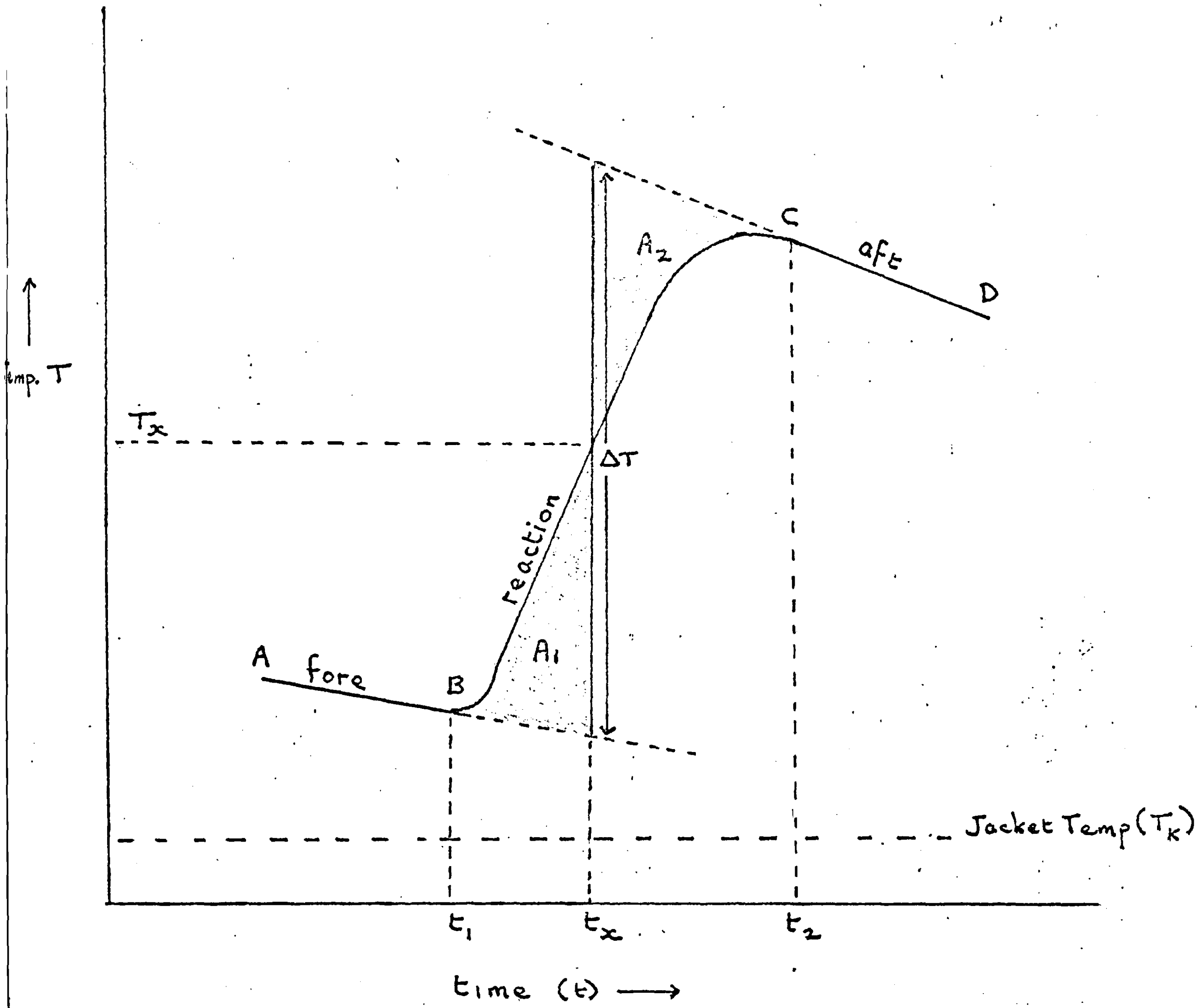


FIG VIII THERMAL LEAKAGE CORRECTION

The curve ABCD represents a typical reaction taking place in the calorimeter.

T_1 and T_2 are the temperatures corresponding to times t_1 and t_2.

The observed rise in temperature of the calorimeter is the difference in temperature at the beginning (T_1) and at the end (T_2) of the reaction period. During this rise, however, heat exchanges with the surroundings occur, so that the correction term C must be added to get the change in temperature ΔT of the calorimeter, due to the reaction alone.

$$\Delta T = T_2 - T_1 + C$$

Assuming that the heat exchange is Newtonian, then the rate of temperature change during the reaction period due only to exchange with the surroundings is given by:

$$\frac{dT}{dt} = \alpha(T - T_k)$$

T_k = jacket (i.e. thermostat) temperature

α = cooling constant of the calorimeter.

Hence the heat correction factor (C) is given by:

$$C = \int_{t_1}^{t_2} \alpha\,(T - T_k)dt$$

The above integral was evaluated using Dikkinson's method.(91)

A line is drawn parallel to the temperature axis through a point t_x, such that the shaded areas A_1 and A_2 between the curve and the lines AB and CD (suitably back-extropolated) are equal. Then:

$$C = \int_{t_1}^{t_2} \alpha (T - T_k)dt = \alpha (T_1 - T_k)(t_x - t_1) + \alpha (T_2 - T_k)(t_2 - t_x)$$

Thus the corrected temperature change ΔT may be obtained simply by back-extrapolating the fore and aft periods to t_x. In a fast reaction ($t_2 - t_1 \sim 30$ seconds) or an electrical calibration, t_x is the mean time of the reaction or heating period. For a slow reaction this is not the case, and the position of t_x depends on the area either side of the perpendicular constructed at $t = t_x$. The position of t_x may then be determined by 'counting squares' or using Dickinson's observation that the temperature (T_x) corresponding to t_x is given approximately by:

$$T_x = 0.60 (T_2 - T_1) + T_1$$

Macleod, in a recent paper(92) has compared several methods of temperature correction and shown that Dickinson's method was acceptable in cases where the required precision was not greater than 0.2%.

The accuracy of the calorimeter

The equation for the enthalpy change is of the form:

$$\Delta H = (\text{electrical energy}) \times \frac{\Delta T \text{ (reaction)}}{\Delta T \text{ (calibration)}}$$

The principle source of error in evaluating ΔH, occurs in the measurement of temperature (i.e. in the back-extrapolation procedure) rather than in measurement of electrical energy, so to a first approximation:

$$\Delta H^1 = \frac{\Delta T^1}{\Delta T} \qquad \frac{\log R_1 - \log R_2}{\log R_3 - \log R_4} = \frac{\log \frac{R_1}{R_2}}{\log \frac{R_3}{R_4}}$$

In a calorimetric run ΔT^1 is made approximately equal to ΔT, so that it is only necessary that the error in $\log \frac{R_1}{R_2}$ be evaluated and then combine errors.

$$\text{let } U = \log \frac{R_1}{R_2}$$

If $U = f(x, y......)$ and the errors in U, x and y..... are $\pm \Delta U$, $\pm \Delta x$, $\pm \Delta y$..... then

$$(\Delta U)^2 = \left\{\frac{\partial U}{\partial x}\right\}^2 \Delta x^2 + \left\{\frac{\partial U}{\partial y}\right\}^2 \Delta y^2 ....$$

$$= \left\{\frac{1}{R_1}\right\}^2 (\Delta R_1)^2 - \left\{\frac{1}{R_2}\right\}^2 (\Delta R_2)^2$$

The error introduced in measuring temperature changes of 0.3°, 0.5° and 1.0° may be calculated. An F.53 thermistor has a sensitivity of ~ 140 Ω per degree and at 25° the resistance is ~ 3650 Ω. The maximum error in measuring resistances is ± 0.5 Ω.

$R_1 = 3650\ \Omega$ and $R_2 = 3690$, 3720 and $3790\ \Omega$ for temperature changes of 0.3, 0.5 and 1.0°C respectively. $R_1 = R_2 = \pm\ 0.5\ \Omega$. By substituting in the above equation the proportional error in U is obtained and by combination of the errors, the proportional error in $\Delta\ H^1$. These uncertainty limits are tabulated (Table XXXV).

TABLE XXXV

Temp. change °C	$\frac{\Delta U}{U}$ %	$\Delta\frac{\Delta H^{\ominus}}{\Delta H^{1}}$
0.3	± 0.42	± 0.60
0.5	± 0.32	± 0.45
1.0	± 0.22	± 0.33

Hence for half a degree temperature change, the total range of Δ H values should be about 1% (this is assuming that the compounds are 100% pure and stable, and the reaction is quantitative).

The accuracy of the calorimeter wascbhecked using two standard calorimetric reactions, one endothermic and one exothermic. The endothermic reaction was the heat of solution of potassium chloride in water. Gunn(125) has questioned the use of this as a standard reaction, because of the wide disagreement of many accurate determinations of this value (the spread of results is approximately 1%). The value recommended by Gunn for the enthalpy of solution of potassium chloride in water (= 4.206 K.cal.mole^{-1} at N = 200) was adopted. The results are recorded in Table XXXVI.

TABLE XXXVI

Enthalpy of solution of potassium chloride in water

N	ΔH_{obs}(K.cal.mole^{-1})	$\Delta H_{N=200}$(K.cal.mole^{-1})
333	4.22	4.22
325	4.20	4.20
148	4.19	4.21
216	4.22	4.22
230	4.21	4.21

ΔH_{obs} mean = 4.212 ± 0.008 K.cal.mole^{-1} at 25°C and N = 200

The standard exothermic reaction was the enthalpy of neutralisation of tris-(hydroxy methyl)- aminomethane (Tham) in 0.1 M hydrochloric acid. The enthalpy value of this reaction is well established.(125) (-7.104 K.cal.mole^{-1} at 25° and N = 1330).

$(CH_2OH)_3C.NH_2 + HCl \longrightarrow (CH_2OH)_3C.NH_3^+ \ ^-Cl$

TABLE XXXVII

N	ΔH_{obs}(K.cal.mole^{-1})
733	-7.13
799	-7.18
862	-7.10
846	-7.13
804	-7.16
921	-7.13

ΔH_{obs} mean = -7.14 ± 0.02 K.cal.mole^{-1} at 25° and N = 830

(The dilution enthalpy for Tham is small).

The experimental procedure and the method of calculation of results has been fully described in a recent thesis.(90)

Section 2. General Techniques

(i) Handling.

All the compounds synthesized in this work were either readily hydrolysable or easily oxidised or both, consequently maximum precautions were taken to avoid contact of these compounds with the air. Operations involving transfer and loading of these compounds into ampoules for the calorimeter, were carried out in a glove-bag filled with dry 'white spot' nitrogen. When derivatives were stable they were generally purified by distillation in an all-glass apparatus equipped with ground glass joints. The majority of distillations were performed under vacuum using a rotary oil pump at a pressure of approximately 0.05mm of mercury. The benzo-2-bora 1, 3 dioxarole derivatives tended to distil and sublime simultaneously at low pressures, blocking the distillation apparatus and preventing any further distillation. This could be overcome by using the distillation apparatus in conjunction with a sublimation unit, or alternatively, distilling at a somewhat higher pressure.

(ii) Elemental Analysis

Carbon, hydrogen, nitrogen and sulphur analyses were carried out by A. Bernhardt, Max-Plank-Institute, Mulheim, Germany.

Chlorine. Easily hydrolysable chlorine,(i.e. that in the form B-Cl) was determined by two methods, (i) aqueous hydrolysis followed by a volumetric titration with standard alkali to a methyl red end point. (ii) the first method did not prove suitable for benzodioxarole derivatives, since on addition of sodium hydroxide to the solution of hydrolysis products, a coloured complex was formed which masked the end point. Hence, after hydrolysis, chlorine was determined gravimetrically, as silver chloride.

Bromine. Bromine was determed by Volhard's method. After hydrolysis of the compound, a known excess of standard silver nitrate solution was added and the excess back-titrated with standard ammenium thiocynate solution, using a ferric salt indicator.

Boron. Several methods of boron analysis were tried during the course of this work. Most of them depend on the fact that boric acid behaves as strong monobasic acid in the presence of excess mannitol, which may be estimated by titration with standard alkali to a phenolphalein end point.

Initially the method of Strahm and Hawthorne(85) was used in which the organo-boron compound was oxidised with trifluoroperoxyacetic acid to boric acid, followed by a fixed p.H potentiometric titration in the presence of mannitol. No consistant results could be obtained with this method. Pierson(86) has suggested a series of graded oxidative reactions for the determination of boron in organo-boron compounds; the boric acid produced was again determined by a fixed p.H technique. In all of Pierson's methods the end point lacked sensitivity. The technique which proved most successful in the analysis of boron was a modification of a method due to Thomas.(87) This method is now described in detail.

The organo-boron compound (~ 0.4g) was digested with concentrated sulphuric acid (~ 10ml) until the sample was completely charred. After cooling, 100 vol. hydrogen peroxide (~ 5ml) was added and the heating continued until the resulting solution became colourless. The solution was cooled and methanol (150ml) was added. The methanol/methyl borate azeotrope was distilled over into a receiver containing water (150ml), where methyl borate hydrolysed to boric acid. After neutralization of the solution to p.H 6.3 with alkali, mannitol (~ 10g) was added to convert boric acid into a stronger monobasic complex which was titrated to p.H 8.5 with standard ($\frac{N}{10}$) sodium hydroxide solution.

Boron in phenylboron dichloride was determined in a different way. It has been shown(88) that a plot of ultraviolet optical density at 219 mμ against concentration of phenylboronic acid (0.01 - 0.1 millimoles) in 50% aqueous methanol, was linear. Thus a known weight of phenylboron dichloride was hydrolysed and the solution made up to the appropriate concentration. The optical density of this solution was measured at the above wavelength and the concentration of phenylboronic acid determined directly from a calibration graph. This method was accurate to ± 1%.

(iii) Spectra

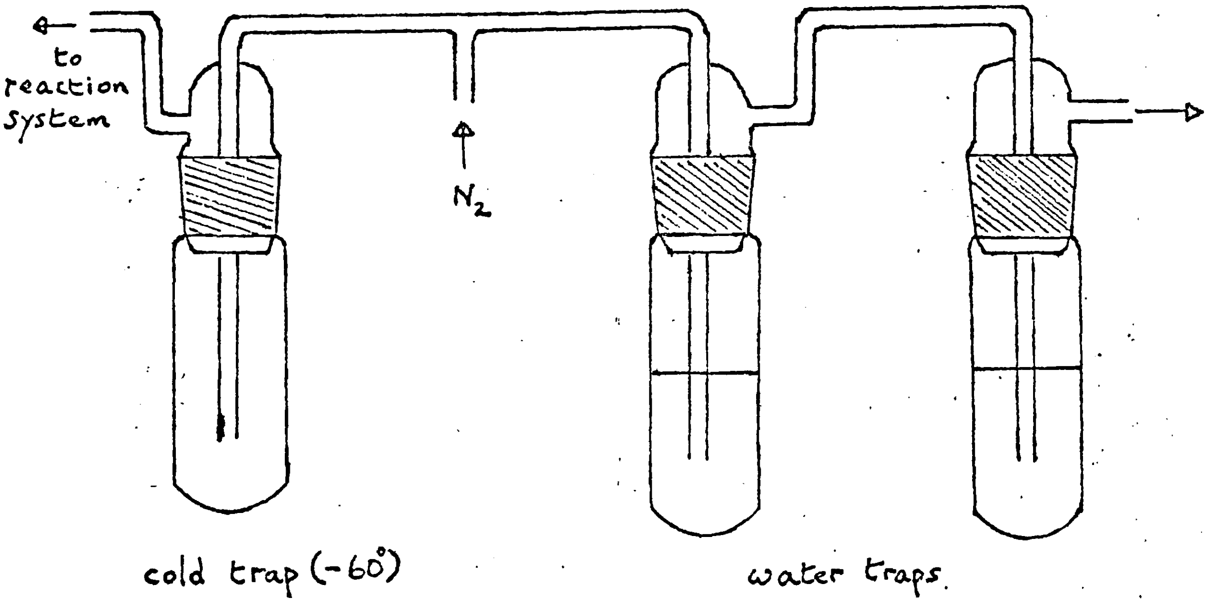
TThe ultraviolet measurements were taken on a Unicam S.P.500 spectrometer, using 1cm. closed cells (silica). The infrared spectra were recorded on a Perkin-Elmer 337 grating infrared spectrometer, using a 10cm. gas cell with KBr optics.

(iv) Refractive Indices

All refractive indices were measured using an Abbé refractometer with a block thermostated at 20° or 25°C and a sodium D line source.

(v) Estimation of Hydrogen Chloride Gas

In a number of the reactions described in Section 3, one of the products is hydrogen chloride gas. If this can be estimated it provides a check on the theoretical stiochiometry of the reaction. The simple apparatus for hydrogen chloride estimation is shown in the diagram.



It consists of three traps in series. The first trap, which is connected directly to the reaction flask is kept at -60°C (chloroform/liquid nitrogen). This prevents any moisture entering the reaction system and also allows hydrogen chloride, formed in the reaction to flow past without being condensed (bp.HCl = $-85^{\circ}C$). The cold trap is connected to two water traps. Nitrogen enters the system at the point shown and flushes out the reaction flask. When the system is closed, it flows in the opposite direction and bubbles through the water traps. In this way the reaction is carried out under an atmosphere of nitrogen. The positive nitrogen pressure also prevents any tendency for water in the traps to 'suck back' when hydrogen chloride is dissolved. After the reaction is completed the solutions in the water traps are mixed and titrated against standard 4N. sodium hydroxide solutions to a methyl red end point. It is unusual for 100% theoretical hydrogen chloride to be estimated because of the high solubility of the gas in methylene chloride (the solvent).

(vi) Preparation of a single crystal of triphenylboron for X-ray analysis

A single crystal of triphenylboron was picked from a crop of crystals which had been obtained by slow crystallisation from a saturated solution of triphenylboron in diethylether. It was loaded into the X-ray tube (a wide-necked glass tube, 0.3mm diameter) in a nitrogen-filled glove bag. A cork stopper prevented oxygen contaminating the crystal after removal of the tube from the glove bag. The X-ray tube was cut to a length of $\sim$ 1cm., using a glowing hot wire and finally sealed by quickly inserting just the tips of both ends of tube into a very small oxygen flame, such that the crystal was not melted.

(vII) Purification of solvents and starting materials

Certain solvents were available commercially but were purified prior to use. 1, 4 dioxan was refluxed over sodium and then distilled through a 50cm. column packed with helices and surrounded by a temperature jacket. A fraction bp. 100-101°/760mm. was collected. The column was also used to distil cyclohexanol, bp. 161°C/760mm. Benzene and diethylether were dried over sodium wire, and methylene chloride, carbon disulphide and petroleum ether (40 - 60°) were dried with 4 Å molecular sieves (BDH).

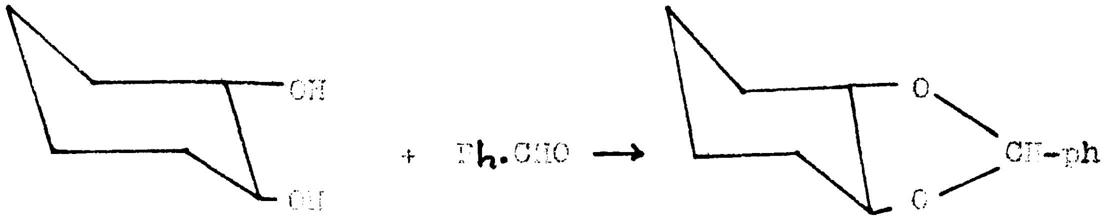
All the solvents were BDH 'Analar grade' except for petroleum-ether, which was 'ordinary grade'. The solvents used in calorimetry were deoxygenated by bubbling dry 'white spot' nitrogen through them.

The majority of starting materials were used in syntheses without further purification, except in the case of:-

1. 4-chlorocatechol, which was found to be partially oxidised. It was purified by a hot filtration followed by recrystallisation from carbon tetrachloride. Mp 85 - 87° lit mp. 90 - 91°.

2. Cyclohexane 1, 3 diol was obtained as an 80% aqueous solution. The water was removed by pumping the sample on an oil-vacuum pump, to yield a very viscous liquid.

3. Cyclohexane 1, 2 diol contained approximately equal mixtures of cis and trans isomers. Several methods of separation of the isomers were tried including fractional crystallisation and solvent extraction, but these were not successful. A chemical separation based on a method by Wilson and Read(89) was finally employed. The cis and trans mixture (72g) was refluxed with benzaldehyde (200ml) for 1 hour in a stremm of carbon dioxide gas. Under these conditions the cis isomer forms a cyclic acetal (benzylidene 1, 2 cyclohexane diol) which was distilled from the reaction mixture (6p. 144-5°/8mm), and the trans isomer does not react.



Trans cyclohexane 1, 2 diol was distilled off unchanged (100 - 120°/17mm) and after crystallisation from benzene had a mp. 99° (lit(89) mp. 103-104°). The cyclic acetal was hydrolysed to the cis diol by boiling for 2 hours with a mixture of N hydrochloric acid (3ml) and acetone (20ml). Some charring occurred during hydrolysis. The yellow solid which precipitated was crystallised from benzene mp. 81-83° lit(89) mp. 98-99°. yield 12.2g, 46% theoretical. (The sample was probably still slightly contaminated with benzaldehyde, but the low yield of cis cyclohexane 1, 2 diol precluded further recrystallisation).

Section 3. Syntheses and Analyses

Triphenylthioborane was synthesised according to Young and Andersons$^{(67)}$procedure. Thiophenol (100g, 3 mol.) was dissolved in benzene (200ml) and a solution of boron trichloride (36g, 1 mol.) in benzene (75ml) was added with stirring, under a dry nitrogen atmosphere. After refluxing the mixture for 8 hours, it was allowed to cool and the solvent was removed. Distillation of the residue several times under reduced pressure, yielded a pale yellow crystalline solid. (42g, 41% theoretical yield). bp. 196-7°/0.1mm. mp.140-3°. lit$^{(67)}$bp. 193-4°/0.02mm. lit$^{(67)}$mp. 129-43°. (found: C, 63.66; H, 4.63; B, 3.27; S, 28.26; calculated for $C_{18}H_{15}BS_3$, C, 63.90; H, 4.47; B, 3.20; S, 28.43)

All of the trialkylthioboranes were prepared by the method of Mikhailov and Bubnov.$^{(68)}$ The alkanethiol (3 mol.) was added to boron trichloride (1 mol.) cooled to -80° (acetone/solid carbon dioxide), with stirring under a dry nitrogen atmosphere. A 1 : 1 complex was obtained which dissolved in the slight excess of thiol. The mixture was allowed to warm up to room temperature. Diethylether (150ml) was added followed by triethylamine (3mol.). When the addition was complete, the mixture was refluxed for 2 hours under a -80° condenser. Triethylamine hydrochloride, which precipitated was filtered off and the solvent removed by pumping. The crude alkylthioborane was purified by vacuum distillation.

<u>n-Amylthioborane</u>. n-pentanethiol (100g, 3.2 mol.) was added to boron trichloride (35g, 1 mol.) (60g. 60% theoretical yield) bp. 146-9°/0.1mm. n_D^{25} = 1.5116. lit.$^{(76)}$ bp = 168-73°/0.2mm. lit.$^{(76)}$ n_D^{24} = 1.5145. (found: C, 56.37; H, 10.43; B, 3.43; S, 29.96; calculated for $C_{15}H_{33}BS_3$: C, 56.23; H, 10.38; B, 3.37; S, 30.02.)

<u>n-butylthioborane</u>. n-butanethiol (100g, 3.3 mol.) was added to boron trichloride (40g, 1 mol.) (35g, 35% theoretical yield). bp. 126-7/0.05mm. n_D^{20} = 1.5203. lit.$^{(77)}$ bp. 150-2°/1mm. lit.$^{(77)}$ n_D^{20} = 1.5205. (found: C, 52.04; H, 9.33; B, 3.99; S, 34.74; calculated for $C_{12}H_{27}BS_3$: C, 51.78; H, 9.75; B, 3.88; S, 34.56).

<u>n-propylthioborane</u>. n-propanethiol (100g, 3.1 mol.) was added to boron trichloride (50g, 1 mol.) (25g, 24% theoretical yield). bp. 102-4°/0.02mm. n_D^{20} = 1.5304, lit.$^{(77)}$ bp. 135-135.5/4mm. lit.$^{(77)}$ n_D^{20} = 1.5312. (found: C, 45.82; H, 8.88; B, 4.70; S, 40.50; calculated for $C_9H_{12}BS_3$: C, 45.75; H, 8.96; B, 4.58; S, 40.71).

<u>Methylthioborane</u>. Methanethiol (100g, 3.3 mol.) was added to boron trichloride (75g, 1.0 mol.) (40g, 39% theoretical yield). bp. 87-8°/10mm. n_D^{20} = 1.5780. lit$^{(68)}$ bp. 93-6/14mm. lit.$^{(68)}$ n_D^{20} = 1.5790. (found: C, 23,47; H, 5.96; B, 7.13;

S, 63.01; calculated for $C_3H_9BS_3$: C, 23.69; H, 5.96; B, 7.11; S, 63.24.)

Phenylboron dichloride was prepared by Gerrard's method.(78) Boron trichloride (50g, 4 mol.) at -80° was added to tetraphenyltin (45g, 1 mol.), and the mixture was allowed to warm to room temperature under a -80° reflux condenser. The rate of reflux gradually increased until a vigorous reaction ensued and the tetraphenyltin dissolved to give a homogenius solution. The solution was refluxed for a further hour. Distillation through a six-inch column packed with helices, gave an initial fraction 105 - 150°/760mm. (mainly stannic chloride) and a second fraction 165-178°/760mm. (phenylboron dichloride). Phenylboron dichloride was purified by redistillation. (50g, 70% theoretical yield). bp. 170-4°/760mm. lit. bp. 73°/15mm. (found: B, 6.8; Cl, 44.4; calculated for $C_6H_5BCl_2$: B, 6.8; Cl, 44.6).

Diphenylboron chloride. The above synthesis was repeated and stannic chloride was removed by distillation at atmospheric pressure. Further tetraphenyltin (34g, 1 mol. based on a 70% reaction yield) was added. After refluxing for approximately 2 hours, stannic chloride was removed and the residue distilled at reduced pressure. Two fractions were obtained; the lower fraction 68-80°/0.05mm. (mainly phenylstannic trichloride) was discarded. The higher fraction, 86-100°/0.05mm. (diphenylboron chloride) was twice recrystallised from petroleum-ether (40-60°) and finally vacuum distilled. (18.5g, 28% theoretical yield). bp. 90-95/0.05mm. Mp. 29-30°. n_D^{20} = 1.6130. lit.(79) bp. 98°/0.1mm. lit.(79) n_D^{20} = 1.6118. (found: Cl, 17.4; calculated for $C_{12}H_{10}BCl$: Cl, 17.7).

Triphenylboron. The preparation of diphenylboron chloride was repeated as above, but the compound was not isolated. Tetraphenyltin (15g, 1 mol. based on a 50% yield of diphenylboron chloride) was added and the mixture refluxed for 2 hrs. and then distilled under reduced pressure. The main fraction was triphenylboron. bp. 144-5°/0.05mm. Crystallisation from diethylether gave a white crystalline solid (42g, 40% theoretical yield) Mp. 148-9° (in vacuo) lit.(80) mp. 151°. (found: C, 88.74; H, 6.31; B, 4.32; calculated for $C_{18}H_{15}B$: C, 89.32; H, 6.20; B, 4.47;)

Phenylboron dibromide. Phenylboron dichloride (44g, 1 mol.) and boron tribromide (52g, 1.05 mol.) were mixed at -80°C. The mixture was warmed to room temperature and then gently refluxed for 30 minutes. Boron trichloride was distilled off and this was collected and estimated. (80% theoretical yield). The residue was distilled under reduced pressure to give a low boiling fraction (42-50°/0.05mm. mainly unreacted phenylboron dichloride)and a fraction boiling at 62-4°/0.5mm. (phenylboron dibromide) , which was initially a colourless liquid and then slowly solidified. It was purified by crystallisation from 40-60° petroleum-ether (29g, 38% theoretical yield) mp. 28-9° (in vacuo). lit.(81) mp.25-28°. (found: Br, 64.8; calculated for $C_6H_5Br_2$: Br, 64.5).

Diphenylborinic anhydride was prepared by controlled stoichiometric hydrolysis of diphenylboron chloride.(Crystalline diphenylboron chloride contained in a vacuum desiccator connected to a water pump was allowed to hydrolyse over a period of 2 weeks). The anhydride was purified by washing with n-pentane mp. 141° lit.(79)mp. 118°. (found: C, 82.6; H, 5.9; B, 6.4; calculated for $C_{18}H_{15}B_3O_3$: C, 83.3; H, 5.8; B, 6.2).

Diphenylboron bromide.(82) Diphenylborinic anhydride (43g, 3.0 mol.) in methylene chloride (120ml) was added to a solution of boron tribromide (31g, 3 mol.) in methylene chloride (50ml) at -80°, over a period of 20 minutes. After the reaction mixture had warmed to room temperature, the solvent was removed and the residue (a rubbery solid) was vacuum distilled. The only fraction obtained was one distilling at 108-112°/0.01mm. lit.(82) 115°/0.05mm. and was identified as diphenylboron bromide (32g, 74% theoretical yield) n_D^{20} = 1.6353 lit.(82)n_D^{20} = 1.635. (found: Br, 32.5; calculated for $C_{12}H_{10}BBr$: Br, 32.7)

N.B. All the above phenylboron compounds (except diphenylborinic anhydride) were prepared under a dry nitrogen atmosphere, and using a -80° cold trap to prevent moisture entering the reaction system.

Tricyclohexylboron has previously been prepared in this laboratory according to Biddulph's method.(83)

Tri-n-hexylborate. n-hexanol (205g, 3 mol.) was mixed with boric acid (41g, 1 mol.) and benzene (150ml) and the mixture refluxed. After refluxing for ~ 12 hours, 3.6ml. of water (100% theoretical) had been collected in a Dean and Stark tube. The solvent was removed and the residue distilled at 0.1mm pressure, yielding a colourless mobile liquid (202g, 96% theoretical yield) bp. 115°/0.1mm.

2-hexoxy-1, 3, 2 hexahydrobenzodioxaborinan.(84) Cyclohexane 1, 3 diol was heated with stirring, with tri-n-hexyl borate. As the reaction proceeded n-hexanol was formed and was distilled off. After 3 hours heating 115g of n-hexanol (87% theoretical) had passed over; the temperature range being 90-160°/760mm. Distillation of the residue yielded a colourless mobile liquid (58g, 44% theoretical) bp. 100-110°/0.1mm. n_D^{21} = 1.4539 lit.(84) bp. 107-20°/0.8mm. lit.(84) n_D^{21} = 1.4390. (found: C, 63.31; H, 10.29; B, 4.72; calculated for $C_{12}H_{23}O_3B$: C, 63.74; H, 10.25; B, 4.78). The trans diol, under these conditions forms a polymeric borate.

Attempted preparation of 2-chloro-1, 3, 2 hexahydrobenzo-dioxaborinan

The hexoxy derivative (34g, 1 mol.) was added to boron trichloride (19g, 1.05 mol.) at -80°C with stirring under a dry nitrogen atmosphere, to give a homogenius straw coloured solution. On warming to room temperature a slow exothermic reaction ensured and the solution turned a deep crimson colour. Distillation of the reaction mixture at reduced pressure was difficult because of the excess frothing which occurred. This was caused by the evolution of a gaseous decomposition product which was detected in the liquid nitrogen trap, but was not identified. The total fraction, boiling over the range 26-50°/0.3mm, was collected and analysed. (found: Cl, 30.2; B, 5.0). This analysis did not correspond to that ofthe expected compound (Cl, 22.1; B, 6.7) and is most likely to be impure hexoxyboron dichloride $C_6H_{13}OBCl_2$ (requires Cl, 38.8; B, 5.9).

Attempted preparation of 2-chloro-1, 3, 2 hexahydrobenzo dioxaborolan (cis)

Cis cyclohexane 1, 2 diol (12g, 1 mol.) was added in suspension in methylene chloride (50ml) to boron trichloride (14g, 1.1 mol.) in methylene chloride (50ml) at -80°C. On warming to room temperature, hydrogen chloride was evolved (56% theoretical) and after removal of the solvent a red syrup remained. This residue failed to distill under reduced pressure and was readily decomposed. (Boron trichloride was detected in the liquid nitrogen traps protecting the pump).

<u>2-chlorobenzo-2-bora 1, 3 dioxarole derivatives</u>

These compounds were all prepared by the same general method.(51)

The substituted catechol (1 mol.) in suspension in methylene chloride (100ml) was added to a solution of boron trichloride (1 mol.) in methylene chloride (20ml) at -80°. A wide-tap dropping funnel was used for the addition and the mixture was stirred under a nitrogen atmosphere. When the homogenius solution warmed to ambient temperature hydrogen chloride was evolved and was estimated by the method already described. The solvent was removed and the product purified by distillation at reduced pressure. Any deviation from this general procedure will be mentioned. The nomenclature used (in Section 3 - Results and Discussion) to describe these compounds will also be used here.

<u>XVIII (R = H)</u> (35g, 50% theoretical yield)

Catechol (45g, 1 mol.) was added to boron trichloride (50g, 1.04 mol.). bp. 71-3°/14mm. mp. 57-8° lit.(51) bp.

64°/10mm. lit.(51)mp. 57° (found: C, 47.24; H, 2.68; B, 6.98; Cl, 23.1; calculated for $C_6H_4O_2BCl$: C, 46.69; H, 2.61; B, 7.00; Cl, 23.0).

XVIII (R = 5-Cl) (28g, 37% theoretical yield)

4-chlorocatechol (54g, 1 mol.) added to boron trichloride (50g, 1.1 mol.) 89% hydrogen chloride estimated. bp. 68-70°/3mm. mp. 39.5 - 40.5°. (C, 39.72; H, 2.06; B, 5.76; Cl (hydrolysable), 19.2; $C_6H_3O_2BCl_2$ requires C, 38.17; H, 1.60; B, 5.73; Cl (hydrolysable), 18.8).

XVIII (R = 5-Me) (33g, 49% theoretical yield)

4-methylcatechol (50g, 1.0 mol.) added to bron trichloride (50g, 1.06 mol.) 90% hydrogen chloride estimated, bp. 81-2°/10mm. mp. 21°, n_D^{25} = 1.5117. (found: C, 48.27; H, 3.63; B, 6.42; Cl, 21.2; $C_7H_6O_2BCl$ requires: C, 49.93; H, 3.59; B, 6.42; Cl, 21.1).

XVIII (R = 4-MeO) (12g, 23% theoretical yield)

3-methoxycatechol (40g, 1 mol.) added to boron trichloride (35g, 1.04 mol.), 78% hydrogen chloride estimated. bp. 92-3°/4.5mm. mp. 53-4°. (found: C, 45.82; H, 4.57; B, 5.83; Cl, 19.1; $C_7H_6O_3BCl$ requires: C, 45.60; H, 3.28; B, 5.86; Cl, 19.2).

The synthesis of this compound was repeated using carbon disulphide as solvent.

3-methoxycatechol (25g, 1.0 mol.) added to boron trichloride (22g, 1 mol.) (23g product obtained 69% theoretical yield). bp. 109°/10mm. (found: C, 46.68; H, 3.96; $C_7H_6O_3BCl$ requires C, 45.60; H, 3.28).

XVIII (R = 5-NO_2) (15g, 40% theoretical yield)

4-nitrocatechol (30g, 1 mol.) was added to boron trichloride (25g, 1.1 mol.). A bright yellow complex was obtained, which on warming the mixture to ambient temperature, dissolved with the evolution of hydrogen chloride gas. The solid residue which remained after removal of the solvent, exploded on distillation at reduced pressure. Hence, the bulk of the sample was crystallised twice from carbon disulphide at -20°, yielding a crop of mushroom coloured needles. mp. 93-4°. (found: C, 35.91; H, 1.66; N, 7.21; B, 5.42; Cl, 17.3; $C_6H_3O_3NBCl$ requires C, 36.15; Cl, 17.8; H, 1.52; N, 7.03; B, 5.42).

The majority of the chemicals used in these preparations were obtained from British Drug Houses (BDH) Ltd., except for the following:-

1. Cyclohexane 1, 2 diol from Aldrich Chemical Company and cyclohexane 1, 3 diol from Robinson Bros. Ltd.
2. Substituted catechols from the Aldrich Chemical Company.
3. Alkenethiols and tetraphenyltin from Eastman-Kodak Ltd.

Section 4. Vapour Pressure Measurements

Two methods were used to determine vapour pressures.

1. *A static method*, which was developed in this laboratory, consisting of an all-glass vapour tensimeter incorporating a spiral gauge. The gauge was used in conjunction with a lamp and scale apparatus to measure any change in vapour pressure, above a compound, with temperature. Although more accurate than the second method described, it was only applicable to compounds having relatively high vapour pressures. (e.g. phenylboron dichloride 15mm at 70°).
2. *A dynamic method* was applied to the majority of compounds investigated in this thesis, and involved the determination of boiling temperature of a liquid at a number of different pressures. The pressure was stabilised by use of a Cartesian manostat placed between the pump (oil-vacuum) and the distillation system, where it operated as a valve. Generally the boiling point was determined for both increasing and decreasing pressure values, as a check on the possible thermal decomposition of the compound. Vapour pressures were measured with a mercury manometer which was accurate to ± 0.5mm, and the pressure range over which experiments were performed was usually 4 - 200mm of mercury. The thermometer was precalibrated against a standard NPL thermometer and was accurate to ± 0.3°C. The change of

vapour pressure (P) with temperature (T) of a liquid is given by the Clausius - Clapeyron equation:-

$$\frac{dP}{dT} = \frac{\Delta Hvap}{T(Vg-Vl)}$$

Hvap = latent heat of vaporisation.

If the volume of the liquid (Vl) is neglected compared to that of the vapour (Vg), and assuming ideal gas behaviour of the latter, then:-

$$\frac{d\ln P}{dT} = \frac{\Delta Hvap}{RT^2} \quad (R = \text{gas constant})$$

or

$$\frac{d\ln P}{d(\frac{I}{T})} = -\frac{\Delta Hvap}{R}$$

If $\log_{10}$ vapour pressure is plotted against $\frac{I}{T}$ a curve is obtained. Generally Hvap is constant over short temperature ranges and a straight line is obtained. The slope of this line multiplied by -2.303R yields a value for the heat of vaporisation. In this work, the slope was more suitably derived from a least squares analysis of the experimental data, which was equated in the form:

$$\log_{10}P(mm) = a - \frac{b}{T^{o}K}$$

where a and b (the slope) are constants.

The system was checked with propionic acid (since this liquid had a convenient boiling range) and the results are compared with literature values(93) in Table XXXVIII.

TABLE XXVIII

Experimental and literature vapour pressures of propionic acid

T^oC	$\log_{10}P$ (expt)	$\log_{10}P$ (lit)
63°	1.54	1.55
73°	1.74	1.75
78°	1.83	1.85
84°	1.94	1.97
90°	2.05	2.08
92°	2.14	2.18
99°	2.21	2.24
111°	2.43	2.44

The average deviation of the above eight observations was ± 2%.

Latent heats of vaporisation derived by the above method refer to the mean temperature of the range over which measurements were taken. These values were 'corrected' to 25° using an empirical equation devised by Watson.(73)

$$\frac{\Delta H^{T}_{vap}}{\Delta H^{298}_{vap}} = \left[\frac{1 - \frac{T}{TC}}{1 - \frac{298}{TC}}\right]^{0.38}$$

TC = critical temperature. The value of TC depends on the type of molecule.

For compounds containing chlorine or sulphur

$$TC = 1.41\ T_B + 66$$

For aromatic compounds not containing chlorine or sulphur

$$TC = 1.027\ T_B + 66.$$

and for all other compounds

$$TC = 1.027\ T_B + 159$$

T_B = normal boiling point (°K).

Section 5. Detailed calorimetric results

All of the calorimetric results quoted in this section are in K.cal.mole^{-1} at a temperature of 25.0 ± 0.1°C unless otherwise indicated. The errors are quoted as twice the standard deviation from a single observation, for five or more observations, and for less than five observations, as the range. N is the mole ratio of calorimetric solvent to compound.

(i) The Thioboranes

Hydrolysis of $(C_6H_5S)_3B$, cryst.

N	ΔH_{obs}
7247	-21.5
4864	-21.3
2929	-22.1
2202	-22.0
2584	-21.6
2618	-21.3
3644	-21.4
3312	-21.8
4607	-21.6

ΔH_{obs}(mean) = -21.6 ± 0.3

Hydrolysis of $(n\text{-}C_5H_{11}S)_3B$, liq.

N	ΔH_{obs}
2933	-24.7
2848	-24.0
3319	-24.2
3142	-23.9
2783	-24.2
2382	-24.3
2305	-24.1
3243	-24.4
2183	-24.1

ΔH_{obs}(mean) = -24.2 ± 0.2

Hydrolysis of $(n\text{-}C_4H_9S)_3B$,liq.

N	ΔH_{obs}
2761	-23.9
2841	-23.8
28[illegible]6	-23.5
3343	-23.3
1974	-23.3
3303	-23.9
2594	-23.6
2369	-24.0

ΔH_{obs}(mean) = -23.7 ± 0.3

Hydrolysis of $(n\text{-}C_3H_7S)_3B$,liq.

N	ΔH_{obs}
2073	-22.6
2708	-22.2
2417	-22.3
2483	-22.8
2325	-22.2
2242	-22.3
2246	-22.0

ΔH_{obs}(mean) = -22.3 ± 0.3

Hydrolysis of $(CH_3S)_3B$,liq

N	ΔH_{obs}
1023	-17.8
1511	-19.9
1362	-17.6
1266	-18.0
1877	-17.3
1715	-17.7
1379	-17.2

ΔH_{obs}(mean) = -17.6 ± 0.3

Solution of $(C_6H_5S)_3B$(cryst) in dioxan

N	ΔH_{obs}
710	-24.8
842	-25.9

ΔH_{obs}(mean) = -25.4 ± 0.5

(ii) The Ø$_{3-n}$ BX$_n$ Series

Hydrolysis of ØBCl$_2$, liq.

N	ΔH_{obs}
2360	-40.7
2425	-40.5
2743	-40.0
4320	-40.6
3620	-40.1
3300	-40.1
2914	-40.2

ΔH_{obs}(mean) = -40.3 ± 0.3

Hydrolysis of ØBBr$_2$,liq (30° ± 0.1°C)

N	ΔH_{obs}
3524	-48.6
4603	-48.8
4002	-48.7
7010	-49.0
4257	-49.0
5350	-49.0

ΔH_{obs}(mean) =-48.8$_5$ ± 0.2

Hydrolysis of Ø$_2$BCl,liq

N	ΔH_{obs}
1644	-16.9 (at 30°C)
2018	-17.3
1433	-17.1$_5$
2054	-17.4
2612	-17.4
1921	-17.0

ΔH_{obs}(mean) = -17.2$_5$ ± 0.1

Hydrolysis of Ø$_2$BBr,liq.

N	ΔH_{obs}
1590	-22.5
1758	-22.5
1677	-21.9
1565	-22.1$_5$
1775	-22.1$_5$
1870	-21.5
1616	-21.6
1824	-21.9

ΔH_{obs}(mean) = -22.0 ± 0.4

Oxidative hydrolysis of $\emptyset_3B$/dioxan in aeb (aqueous excess base)

10^2N_1	10^4N_2	Q(cal)	ΔH_2
1.552	3.9010	-143.3	-276.6
1.479	2.4837	-101.9	-274.4
1.899	4.1719	-159.0	-277.4
2.052	4.5474	-173.5	-278.6
1.184	4.2442	-144.5	-276.9
1.249	4.7270	-157.7	-273.3
1.578	4.7850	-167.9	-275.8

Where N_1 and N_2 are the number of moles of dioxan and triphenylboron respectively.

ΔH_2(mean) = -276.1 ± 1.8 (enthalpy of reaction of $\emptyset_3B$ in aeb)

Solution of $\emptyset_3B$ in 1, 4 dioxan

N	ΔH_{obs}
654	3.2
740	3.4
795	3.3
849	3.1
632	3.3_5

ΔH_{obs}(mean) = 3.3 ± 0.13

Solution of 1, 4 dioxan in aeb

N	ΔH_{obs}
310	-2.3
317	-233
332	-2.3
409	-2.3

ΔH_{obs}(mean) = -2.3

Solution of ϕ_3B in benzene

N	ΔH_{obs}
628	4.1
562	3.8
550	4.2
427	4.2
533	3.9
450	4.2

ΔH_{obs}(mean) = 4.1 ± 0.2

Solution of cyclohexanol in aeb

N	ΔH_{obs}
313	-1.97
285	-1.93
296	-1.97
350	-2.01
266	-2.00

ΔH_{obs}(mean) = -1.98 ± 0.3

Oxidative hydrolysis of $(C_6H_{11})_3B$/cyclohexanol in a.e.b.

10^2N_1	10^4N_2	Q(cal)	ΔH_2
3.2278	3.1851	-149.8	-296.6
2.7941	3.9304	-163.4	-274.9
2.7221	4.3454	-173.5	-275.1
2.8519	4.7258	-186.4	-274.9
3.2218	3.9266	-169.9	-270.2
2.6420	3.5962	-149.5	-270.3
2.3224	3.2005	-133.4	-273.1

N_1 and N_2 are the number of moles of cyclohexanol and triphenylboron respectively.

ΔH_2(mean) = -272.6 ± 2.3 (enthalpy of reaction of $(C_6H_{11})_3B$ in a.e.b.)

Solution of $(C_6H_{11})_3B$ in cyclohexanol

N	ΔH_{obs}
955	1.9

Oxidative hydrolysis of ϕ_2BCl,liq. in a.e.b.

N	ΔH_{obs}
8563	-218.3
10,178	-217.0
15,673	-217.9
11,392	-214.1
10,055	-216.2
8010	-214.3

$\Delta H_{obs}(\text{mean}) = -216.3 \pm 1.8$

(iii) The substituted 2-chlorobenzo-2-bora 1, 3 dioxarole derivatives

These compounds are identified, as in Section 3 - results and discussion, by the numeral XVIII, followed by the substituent.

Hydrolysis of XVIII (R = H),cryst.

N	ΔH_{obs}
1883	-22.4
2029	-22.6
1970	-22.6
2444	-22.8
1997	-22.6
2820	-23.0

ΔH_{obs}(mean) = -22.7 ± 0.2

Hydrolysis of XVIII (R = 5-Cl),cryst.

N	ΔH_{obs}
1591	-23.65
1368	-23.65
1522	-23.6
1603	-23.9

ΔH_{obs}(mean) = -23.7 ± 0.15

Hydrolysis of XVIII (R = 5-Me),liq.

N	ΔH_{obs}
1315	-26.5
1274	-26.8
1843	-26.7
1936	-26.6

ΔH_{obs}(mean) = -26.65 ± 0.15

Hydrolysis of XVIII (R = 4-MeO),cryst.

N	ΔH_{obs}
1645	-22.8
2733	-22.45
1472	-22.75
2336	-22.3

ΔH_{obs}(mean) = -22.6 ± 0.25

Hydrolysis of XVIII ($R = 5\text{-}NO_2$),cryst

N	ΔH_{obs}
1659	-23.5
2445	-23.7
2686	-23.5
2716	-23.4
2324	-23.3

ΔH_{obs}(mean) = 23.5 ± 0.15

Sol. of XVIII($R=5\text{-}NO_2$),cryst. in benzene

N	ΔH_{obs}
325	4.78
294	4.54
278	4.64

ΔH_{obs}(mean) = 4.6_5 ± 0.1

Solution of XVIII ($R = 4\text{-}MeO$),cryst.in benzene

N	H_{obs}
217	4.67
183	4.81

ΔH_{obs}(mean) = 4.74 ± 0.07

Solution of XVIII ($R = H$), cryst. in benzene

N	ΔH_{obs}
164	4.30
187	4.32

ΔH_{obs}(mean) = 4.31 ± 0.005

Solution of XVIII (R = 5-Me) cryst. in benzene

N	ΔH_{obs} (at 20°C)
120	3.97
159	4.18
204	4.09
194	4.28

ΔH_{obs}(mean) = 4.13 ± 0.15

Solution of catechol (cryst.) in water

N	ΔH_{obs}
866	3.64
796	3.69
693	3.55
815	3.71

ΔH_{obs}(mean) = 3.65 ± 0.05

Sol. of 4-chlorocatechol(cryst) in water

N	ΔH_{obs}
571	4.30
627	4.07
826	4.23
626	4.28

ΔH_{obs}(mean) = 4.2 ± 0.1

Sol. of 4-methylcatechol(cryst) in water

N	ΔH_{obs}
1138	3.61
1048	3.56
594	3.70
632	3.71

ΔH_{obs}(mean) = 3.65 ± 0.1

Sol. of 4-nitrocatechol(cryst) in water

N	ΔH_{obs}
944	4.77
1087	4.69
1199	4.78
1096	4.81

ΔH_{obs}(mean) = 4.76 ± 0.05

Solution of 3-methoxycatechol (cryst.) in water

N	ΔH_{obs}
1292	3.27
1436	3.29

$\Delta H_{obs}(\text{mean}) = 3.28 \pm 0.01$

Hydrolysis of 2-hexoxy 1, 3, 2-hexahydrobenzodioxaborolan, liq.

N	ΔH_{obs}
1765	-14.5_5
2110	-14.8
1828	-14.7
1632	-15.0
1386	-14.8

$\Delta H_{obs}(\text{mean}) = -14.8 \pm 0.2$

Solution of cyclohexane 1, 2 diol (cis and trans), cryst. in water

N	ΔH_{obs}
724	0.87
730	0.95

$\Delta H_{obs}(\text{mean}) = 0.91 \pm 0.04$

Solution of boric acid (cryst) in the following equimolar solutions

Solution	N	ΔH_{obs}	
Catechol-HCl	525	5.17	5.24 ± 0.1
	483	5.30	
4-methylcatechol-HCl	518	5.17	5.23 ± 0.1
	552	5.28	
4-chlorocatechol-HCl	497	5.09	
3-methoxycatechol-HCl	600	5.28	
4-nitrocatechol-HCl	571	5.26	

Solution of boric acid (cryst) in the following 2 x molar solutions

Solution	N	ΔH_{obs}	
Catechol-HCl	910	5.24	5.28 ± 0.02
	935	5.30	
4-methylcatechol-HCl	913	5.28	5.22 ± 0.06
	939	5.16	
4-chlorocatechol-HCl	782	5.29	
3-methoxycatechol	962	5.31	
4-nitrocatechol	920	5.20	

Section 6. Detailed vapour pressure data

i. The alkylthioboranes

n-amylthioborane

T°C	P(mm)
204.0	5
212.5	8.5
220.5	12
225.5	1[illegible]
231.5	19
226.5	17
215.5	10
207.5	7

n-butylthioborane

T°C	P(mm)
166.5	4
194.0	16
198.5	18
214.5	39
218.0	44
228.5	64
235.0	86

n-propylthioborane

T°C	P(mm)
150.0	8.5
175.5	27
181.5	36
186.5	43
194.5	64
209.0	90
192.0	58
164.5	17
143.0	5.5
137.5	4

(ii) $\phi_{3-n}BX_n$ Series

Phenylboron dibromide

T°C	P(mm)
160.0	218
152.0	182
145.0	144
142.0	126
137.0	103
128.0	76
118.0	64

Diphenylboron bromide

T°C	P(mm)
162.0	11
176.0	21
182.0	27
192.0	38
199.0	49
205.5	61
211.5	72
219.5	90
224.5	101
232.5	126
241.5	157
231.0	115
223.0	94

The vapour pressure variation with temperature of phenylboron dichloride, diphenylboron chloride and triphenylboron have been measured previously in this laboratory.

(ii) The 2-chlorobenzo-[illegible] 1, 3 dioxarole derivatives

These compounds are identified as in Section 5.

XVIII (R = H)

T°C	P(mm)
72.0	14
76.5	19
82.0	26
88.0	36
91.5	42
97.0	54
103.0	69
109.0	88
120.0	134
117.0	120
113.5	105

XVIII (R = 5-Me)

T°C	P(mm)
65.0	4
79.0	9
87.0	13
92.0	18
101.0	27
109.0	38
114.5	48
120.0	59
127.0	79
97.0	23
82.0	10

XVIII (R = 5-Cl)

T°C	P(mm)
99.0	18
111.0	33
121.0	48
125.0	56
134.0	70
142.0	91
148.0	111
145.5	102
138.5	78
86.0	9
75.5	5
95	14

XVIII (R = 4-MeO)

T°C	P(mm)
85.0	4
97.5	7
109.0	11
113.5	14
116.5	17
125.5	26
134.5	36
142.0	50
106.0	9.5

2-hexoxy 1, 3, 2-hexahydrobenzodioxaboralan

T°C	P(mm)
136.0	5
150.0	9
157.0	13
166.0	18
176.0	31
184.0	40
126.5	3
171.5	25
187.0	43

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THERMOCHEMISTRY OF THE TRIALKYLTHIOBORANES AND TRIPHENYLTHIOBORANE

Thermochemistry of the Trialkylthioboranes and Triphenylthioborane

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Values for the standard enthalpies of formation and transition (condensed phase to gas) are reported for the series $(RS)_3B$, where R = CH_3, n-C_3H_7, n-C_4H_9, n-C_5H_{11} and C_6H_5. The energy of the boron-sulphur bond in these compounds is evaluated and is found to be nearly constant except for trimethylthioborane.

The standard enthalpy of formation and the energy of the boron-sulphur bond in triethylthioborane have been reported.[1] That work has been extended to include those members of the series $(RS)_3B$ for which R is CH_3, n-C_3H_7, n-C_4H_9, n-C_5H_{11} and C_6H_5. Sufficient members of the series have been investigated so that the standard enthalpy of formation of any symmetric alkylthioborane containing unbranched carbon chains may be estimated. Extension to thioboranes containing branched acyclic chains should be simple in view of the extensive and accurate bond energy schemes for hydrocarbons.[2] The enthalpies of formation of the compounds were derived from their enthalpies of hydrolysis, determined with the aid of a conventional solution calorimeter.

EXPERIMENTAL

PREPARATION OF COMPOUNDS

TRIPHENYLTHIOBORANE.—This was prepared according to the method of Young and Anderson[3] by condensing thiophenol (3 mol.) and boron trichloride (1 mol.) in benzene solvent. Purification by vacuum distillation yielded a pale-yellow solid, b.p. 196-7°/0·1 mm, m.p. 140-143°, lit.[3] b.p. 193-4°/0·02 mm, lit.[3] m.p. 129-43° (found: C, 63·66; H, 4·63; B, 3·27; S, 28·26; calc. for $C_{18}H_{15}BS_3$: C, 63·90; H, 4·47; B, 3·20; S, 28·43).

TRIALKYLTHIOBORANES.—These were prepared according to the method of Mikhailov and Bubnov[4] by condensing the appropriate alkyl thiol (3 mol.) with boron trichloride (1 mol.) in ether solvent, and abstracting the liberated hydrogen chloride with triethylamine. The physical constants and analyses are given below.

n-AMYLTHIOBORANE, b.p. 146-9°/0·1 mm, n_D^{25} = 1·5116, lit.[5] b.p. 168-173°/0·2 mm, lit.[5] n_D^{24} = 1·5145 (found: C, 56·37; H, 10·43; B, 3·43; S, 29·96; calc. for $C_{15}H_{33}BS_3$: C, 56·23; H, 10·38; B, 3·37; S, 30·02).

n-BUTYLTHIOBORANE, b.p. 126-7°/0·05 mm, n_D^{20} = 1·5203, lit.[6] b.p. 150-2°/1 mm, lit.[6] n_D^{20} = 1·5205 (found: C, 52·04; H, 9·33; B, 3·99; S, 34·74; calc. for $C_{12}H_{27}BS_3$: C, 51·78; H, 9·75; B, 3·88; S, 34·56).

n-PROPYLTHIOBORANE, b.p. 102-4°/0·02 mm, n_D^{20} = 1·5304, lit.[6] b.p. 135-135·5/4 mm, lit.[6], n_D^{20} = 1·5312 (found: C, 45·82; H, 8·88; B, 4·70; S, 40·50; calc. for $C_9H_{12}BS_3$: C, 45·75; H, 8·96; B, 4·58; S, 40·71).

METHYLTHIOBORANE, b.p. 87-8°/10 mm, $n_D^{20} = 1{\cdot}5780$, lit.[4] b.p. 93-6/14 mm, lit.[4] $n_D^{20} = 1{\cdot}5790$ (found: C, 23·47; H, 5·96; B, 7·13; S, 63·01; calc. for $C_3H_9BS_3$: C, 23·69; H, 5·96; B, 7·11; S, 63·24).

ANALYSES AND HANDLING

Boron analyses were performed by degrading the compound with approximately 10 ml of concentrated sulphuric acid and 5 ml of aqueous hydrogen peroxide (100 volume) followed by warming. Excess methanol was added and the trimethylborate+methanol azeotrope distilled into water; boric acid was estimated by the usual volumetric technique. Carbon, hydrogen and sulphur analyses were by Bernhardt, Max-Planck-Institut. All compounds were handled in nitrogen-filled glove bags and stored in the dark.

CALORIMETER

The calorimeter was of the constant-temperature-environment type, fully immersed in a thermostat controlled to 25° ±0·01°C. A full description may be found elsewhere.[7] The precision and accuracy were checked by two standard reactions, one exothermic and the other endothermic. For the enthalpy of neutralization of tris-(hydroxymethyl)-amino-methane (THAM) in excess 0·1 M HCl, the mean of six determinations was $-7{\cdot}14 \pm 0{\cdot}02$ kcal mole^{-1} at 25°C and $N = 830$ (lit.[8] $-7{\cdot}104$ kcal mole^{-1} at 25°C and $N = 1330$). The dilution enthalpy for THAM is very small. For the intergral enthalpy of solution of KCl in water, $\Delta H_S = 4{\cdot}212 \pm 0{\cdot}008$ at 25° and $N = 200$ (lit.[9] 4·206 kcal mole^{-1} at 25° and $N = 200$). N is the mole ratio of water to solute. All enthalpies are quoted in terms of 1 cal = 4·1840 abs. J.

ENTHALPIES OF TRANSITION

The enthalpies of transition were determined by a dynamic distillation technique, establishing an equilibrium between liquid and vapour and stabilizing the pressure with a Cartesian monostat. The thermometer was pre-calibrated and temperature measurement was accurate to ±0·03°C. The pressure range over which the esperiments were performed was usually 5 to 120 mm Hg, and individual pressure measurements were accurate to ±1·0 mm Hg. This method was checked using propionic acid [10] and the average deviation of eight observations over 63-111°C was ±2 %. The experimental data are represented in the form,

$$\log_{10} P_{\text{mm}} = a - (b/T°\text{K}).$$

TABLE 1

compound	range (T°C)	a	$10^{-3}\,b$	$\Delta H(T: l \rightarrow g)$ kcal mole^{-1}	$\Delta H(298: l \rightarrow g)$ † kcal mole^{-1}
$(CH_3S)_3B$	30-120	8·964	2·695	12·3	12·9 ±0·2
$(C_2H_5S)_3B$	—	—	—	—	14·6 ±0·5 [1]
$(n\text{-}C_3H_7S)_3B$	150-210	10·32	3·98	18·2	20·8 ±0·5
$(n\text{-}C_4H_9S)_3B$	167-230	10·55	4·38	20·0	22·9 ±0·5
$(n\text{-}C_5H_{11}S)_3B$	173-230	10·86	4·82	$22{\cdot}0_5$	25·0 ±0·5
$(C_6H_5S)_3B$	—	—	—	—	26·0* ±1·5

* estimated from a graph of molecular weight against $\Delta H(298: l \rightarrow g)$ of $(RS)_3B$.

† estimated from $\Delta H(T: l \rightarrow g)$ using Watson's equation (K. M. Watson, *Ind. Eng. Chem.*, 1931, **23**, 362).

RESULTS

Trialkylthioboranes are readily hydrolyzed according to

$$(RS)_3B + 3H_2O \rightarrow H_3BO_3 + 3RSH.$$

The thiols produced are slightly water-soluble and therefore all hydrolyses were performed in saturated solutions of the thiols; in this way the thiols produced by hydrolysis can be assumed to be in their standard states. We have, therefore,

$$(\mathrm{RS})_3\mathrm{B}(l \text{ or cryst.}) + (n+3)\mathrm{H_2O}(l) \rightarrow 3\mathrm{RSH}(l \text{ or } g) + \mathrm{H_3BO_3}\,.\,n\mathrm{H_2O}, \qquad \Delta H_{\mathrm{obs.}},$$

from which

$$\Delta H_f^0[(\mathrm{RS})_3\mathrm{B}, l \text{ or cryst.}] = \Delta H_f^\circ][\mathrm{H_3BO_3}.n\mathrm{H_2O}] + 3\Delta H_f^\circ[\mathrm{RSH}, l \text{ or } g] - 3\Delta H_f^\circ[\mathrm{H_2O}, l] - \Delta H_{\mathrm{obs}}.$$

TABLE 2

compound	N	ΔH_{obs} kcal.mole^{-1} (at 25·0±0·1°C)	compound	N	ΔH_{obs} kcal mole^{-1} (at 25·0±0·1°C)
$(\mathrm{C_6H_5S})_3\mathrm{B}$	7247	−21·5	$(\mathrm{n\text{-}C_5H_{11}S})_3\mathrm{B}$	2933	−24·7
	4864	−21·3		2848	−24·0
	2929	−22·1		3319	−24·2
	2202	−22·0		3142	−23·9
	2584	−21·6		2783	−24·2
	2618	−21·3		2382	−24·3
	3644	−21·4		2305	−24·1
	3312	−21·8		3243	−24·4
	4607	−21·6		2183	−24·1
	mean	−21·6±0·3		mean	−24·2±0·2
$(\mathrm{n\text{-}C_4H_9S})_3\mathrm{B}$	2761	−23·9			
	2841	−23·8	$(\mathrm{n\text{-}C_3H_7S})_3\mathrm{B}$	2073	−22·6
	2866	−23·5		2708	−22·2
	3343	−23·3		2417	−22·3
	1974	−23·3		2483	−22·8
	3303	−23·9		2325	−22·2
	2594	−23·6		2242	−22·3
	2369	−24·0		2346	−22·0
	mean	−23·7±0·3		mean	−22·3±0·3
$(\mathrm{CH_3S})_3\mathrm{B}$	1023	−17·8			
	1511	−17·9			
	1362	−17·6			
	1266	−18·0			
	1877	−17·3			
	1715	−17·7			
	1379	−17·2			
	mean	−17·6±0·3			

TABLE 3

	$(\mathrm{CH_3S})_3\mathrm{B}$	$(\mathrm{C_2H_5S})_3\mathrm{B}$	$(\mathrm{n\text{-}C_3H_7S})_3\mathrm{B}$	$(\mathrm{n\text{-}C_4H_9S})_3\mathrm{B}$	$(\mathrm{n\text{-}C_5H_{11}S})_3\mathrm{B}$	$(\mathrm{C_6H_5S})_3\mathrm{B}$
ΔH_f° cryst. 25°C	—	—	—	—	—	+15·1±0·9
$\Delta H_f^\circ(l.)$ 25°C	−50·3±0·6	−82·8±0·5 †	−100·8±0·6	+117·1±0·9	−135·7±1·2	—
$\Delta H_f^\circ(g)$ 25°C	−37·4±0·6	−68·2±0·7 †	−80·0±0·8	−94·2±1·0	−110·7±1·3	+45·1±1·8 *

* assuming the enthalpy of fusion of $(\phi\mathrm{S})_3\mathrm{B}$ is the same as for $\phi_3\mathrm{B}$ (4 kcal mole^{-1}), ($\phi = \mathrm{C_6H_5}$).

† recalculated using current ancillary thermodynamic data.

For the hydrolysis of trimethylthioborane, the product (methanethiol) was gaseous. Any thermal effect due to the evolution of this gas, e.g., direct thermal transfer or from vaporization of water, was assumed negligible in comparison with the heat quantities being measured.

The error quoted for the means is twice the standard deviation of a single observation.

Combining the data of tables 1 and 2, the standard enthalpies of formation of the compounds are collected in table 3.

The ancillary thermodynamic data used (all in kcal mole^{-1}) were:

$$\Delta H_f^\circ[\mathrm{H_2O},l] = -68{\cdot}32\ ^{12};$$

$$\Delta H_f^\circ[\mathrm{H_3BO_3},c] = -261{\cdot}7\pm0{\cdot}2\ ^{13};$$

$$\Delta H_f^\circ[\mathrm{H_3BO_3}aq.] = -256{\cdot}5\pm0{\cdot}2\ ^{13};$$

(the heat of dilution of boric acid in water is negligible).[14]

$$\Delta H_f^\circ[\mathrm{CH_3SH},g] = -5{\cdot}46\pm0{\cdot}14\ ^{15};$$

$$\Delta H_f^\circ[\mathrm{C_2H_5SH},l] = -17{\cdot}62\pm0{\cdot}11\ ^{15};$$

$$\Delta \mathrm{H}_f^\circ[\mathrm{n\text{-}C_3H_9SH},l] = -23{\cdot}84\pm0{\cdot}16\ ^{15};$$

$$\Delta H_f^\circ[\mathrm{n\text{-}C_4H_9SH},l] = -29{\cdot}76\pm0{\cdot}28\ ^{15};$$

$$\Delta H_f^\circ[\mathrm{n\text{-}C_5H_{11}SH},l] = -36{\cdot}11\pm0{\cdot}40\ ^{15};$$

$$\Delta H_f^\circ[\phi\mathrm{SH},l] = 15{\cdot}02\pm0{\cdot}27.^{15}$$

Enthalpies of formation of simple alkane thiols have recently been reviewed.[16]

DISCUSSION

A least-square analysis of the data for ethyl, n-propyl, n-butyl and n-amylthioboranes yields the following equations for the standard enthalpies of formation at 25°C of symmetric trialkylthioboranes,

$$-\Delta H_f^\circ[\mathrm{(RS)_3B},l] = [17{\cdot}50\pm0{\cdot}12]n+[47{\cdot}85\pm0{\cdot}44],$$

$$-\Delta H_f^\circ[\mathrm{(RS)_3B},g] = [15{\cdot}11\pm0{\cdot}16]n+[37{\cdot}49\pm0{\cdot}60],\ \text{kcal mole}^{-1},$$

where n is the number of carbon atoms in R. Bond energies E in these compounds were evaluated from a knowledge of the standard enthalpies of formation of the gaseous thioboranes ($\Delta H_f^\circ(g)$), the enthalpies ΔH_a of atomization of the constituent elements and the equation

$$\sum E = \sum \Delta H_a - \Delta H_f^\circ(g),$$

all thermodynamic data being for 25°C. The enthalpies of atomization [17] used in the calculations were C($170{\cdot}9\pm0{\cdot}45$), H($52{\cdot}10\pm0{\cdot}001$), B($132{\cdot}8\pm4{\cdot}0$) and S($66{\cdot}7\pm0{\cdot}5$) in kcal g atom^{-1} at 25°C. Two bond energy schemes were used: (i) that proposed by Laidler,[18] and Mackle [19] *et al.* (L.M. scheme) and (ii) the Allen [20] scheme. The L.M. scheme assumes different values for the C—H bond energy dependent on whether the H is primary, secondary or tertiary, and a fixed value for the C—C bond energy. The numerical values of these bond energies and those for $E(\mathrm{C{-}H})_{\mathrm{ar}}$, $E(\mathrm{C{-}C})_{\mathrm{ar}}$, $E(\mathrm{C}_{sp^3}\mathrm{{-}S})$ and $E(\mathrm{C}_{sp^2}\mathrm{{-}S})$ were taken from Mackle [19] *et al.* The Allen scheme assumes a constant value for $E(\mathrm{C{-}H})$ but takes account of non-bonded interactions. Applying the Allen scheme to alkylthioboranes,

$$\sum \Delta H_a - \Delta H_f^\circ(g) = 3B_{\mathrm{CS}}+a_2B_{\mathrm{CH}}+a_3B_{\mathrm{CC}}+3B_{\mathrm{BS}}+a_4\Gamma_{\mathrm{CCC}}+3\Gamma_{\mathrm{SBS}}+3\Gamma_{\mathrm{BSC}}+a_5\Gamma_{\mathrm{CCS}} + \Delta^{\mathrm{B}}_{\mathrm{SSS}},$$

where B is the " effective " Allen bond energy, Γ are the magnitude of 1,3 interactions and the coefficients a_i the frequency of occurrence. Using Skinner and Pilcher's collated data [2] (after adjustment to $\Delta H_f^\circ[\mathrm{S},g] = 66{\cdot}7$) for B_{CH}, B_{CS}, B_{CC}, Γ_{CCC} and Γ_{CCS} we evaluate the composite term,

$$W = (B_{\mathrm{BS}}+\Gamma_{\mathrm{SBS}}+\Gamma_{\mathrm{BSC}}+\tfrac{1}{3}\Delta^{\mathrm{B}}_{\mathrm{SSS}}).$$

The error in a bond energy term depends on (i) the precision of the standard enthalpy of formation of the compound and the compounds from which the ancillary bond energies were determined, and (ii) the precision of the atomization energies of the two atoms constituting the bond each divided by their formal valency. For the alkylthioboranes, term (i) contributes about ±1·1 kcal, and term (ii), ±1·3 kcal, giving a net error of ±1·7 kcal (2·5 for R = C_6H_5). The bond energies in the fourth column are derived from ΔH_f°[RS,*g*] where it is known.[19] The error on these *E* data is too large for the results to be significant except that the good agreement with the other data imply that the errors assigned to the ΔH_f°[RS,*g*] data (±5 kcal mole^{-1}) were too large.

TABLE 4

R in $(RS)_3B$	*E*(B—S)(LM) kcal	*W* (Allen) kcal	*E*(B—S) from ΔH_f°[RS,*g*] kcal
CH_3	85·0	87·2	87·4 ±5
C_2H_5	90·4	91·8	92·5 ±5
n-C_3H_9	89·4	90·8	
n-C_4H_9	89·3	90·7	
n-C_5H_{11}	89·9	91·3	
C_6H_5	89·8	—	

There is a marked disparity in the boron-sulphur bond energy in methylthioborane and its homologues (~5 kcal). A corresponding difference also occurs in the trialkyl borates, $(RO)_3B$, (~12 kcal). If this is due to an inductive effect then it appears that oxygen is more efficient in transmitting this effect than sulphur; arguments based on size support this idea. The fact that the alkylthio-boron bond energy is the same as the arylthio-boron bond energy implies that the phenyl substituents do not effect the electronic character of the B—S bond. This supports Mackle's evidence [19] that there is no thermodynamic stabilization resulting from conjugation between a sulphur atom and an adjacent delocalized electronic system.

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THERMOCHEMISTRY OF TRIPHENYLBORON, TRICYCLOHEXYLBORON AND SOME PHENYLBORON HALIDES

Thermochemistry of Triphenylboron, Tricyclohexylboron and some Phenylboron Halides

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The standard enthalpies of formation and transition (from condensed phase to gas) are reported for the following compounds: triphenylboron, tricyclohexylboron, diphenylboron chloride and bromide, phenylboron dichloride and dibromide. The boron-phenyl bond strength is determined; its value increases with successive replacement of phenyl by halogen, and is discussed in terms of structural features.

Thermodynamic data for organo-boron compounds are sparse, especially for compounds containing the aromatic nucleus. The thermochemistry of phenylboronic and borinic acids has been reported.[1] Using these data and a conventional reaction calorimeter we report the thermochemistry of some phenylboron halides via their hydrolyses. For triphenyl and tricyclohexylboron, oxidative hydrolyses are studied.

EXPERIMENTAL

SYNTHESIS OF COMPOUNDS

PHENYLBORON DICHLORIDE.—Boron trichloride and tetraphenyl tin were mixed in 1 : 4 mole ratio according to $\phi_4\mathrm{Sn}+4\mathrm{BCl}_3 \rightarrow 4\phi\mathrm{BCl}_2+\mathrm{SnCl}_4$, following Gerrard[2] *et al.* Fractionation through a 6 in. column packed with helices gave a middle fraction of phenylboron dichloride (70 % theoretical yield) b.p. 170-4°/760 mm; lit.[2] b.p. 73°/15 mm (found: B, 6·8; Cl, 44·4; calc. for $C_6H_5BCl_2$: B, 6·8; Cl, 44·6 %).

DIPHENYLBORON CHLORIDE.—The above synthesis was repeated and stannic tetrachloride removed by distillation at atmospheric pressure. Further tetraphenyl tin was added to the crude phenylboron dichloride according to $\phi_4\mathrm{Sn}+4\phi\mathrm{BCl}_2 \rightarrow 4\phi_2\mathrm{BCl}+\mathrm{SnCl}_4$. Stannic chloride and phenylstannic chlorides were removed by distillation at atmospheric pressure (boiling range, 115-200°/760 mm). Distillation of the residue yielded a middle fraction b.p. 96-100°/0·1 mm which on redistillation gave diphenylboron chloride (55 % theoretical yield), b.p. 94-96°/0·1 mm; mp. 29-30°, $n_D^{20} = 1{\cdot}6118$; lit.[3] b.p. 98°/0·1 mm, $n_D^{20} = 1{\cdot}6118$ (found: Cl, 17·4; calc. for $C_{12}H_{10}BCl$; Cl, 17·7 %).

TRIPHENYLBORON.—This compound is extremely sensitive to aerial oxidation and commercial samples were extensively oxidized. The above synthesis was repeated and further tetraphenyltin was added according to $\phi_4\mathrm{Sn}+4\phi_2\mathrm{BCl} \rightarrow 4\phi_3\mathrm{B}+\mathrm{SnCl}_4$. Distillation yielded triphenylboron (80 % theoretical yield), b.p. 203°/15 mm. Crystallization from sodium-dried diethyl ether gave a white crystalline solid m.p. 148-149° (*in vacuo*), lit. m.p.[4] 151°, (found: B, 4·32; calc. for $C_{18}H_{15}B$: B, 4·47 %). Rigorous precautions to exclude oxygen are necessary during handling.[5]

PHENYLBORON DIBROMIDE.—Phenylboron dichloride and boron tribromide were mixed at −80°C according to $3\phi\mathrm{BCl}_2+2\mathrm{BBr}_3 \rightarrow 3\phi\mathrm{BBr}_2+2\mathrm{BCl}_3$. On warming to room temperature, boron trichloride (80 % theoretical) was removed. The residue was distilled under reduced pressure and a low-boiling fraction (mainly unreacted phenylboron dichloride) discarded. The second fraction, b.p. 62-64°/0·5 mm, initially a colourless liquid, slowly solidified and was purified by crystallization from 40/60 petroleum ether (38 % theoretical yield), m.p. 28-9°; lit.[6] m.p. 25-28° (found: Br, 64·8; calc. for $C_6H_5BBr_2$: Br, 64·5 %).

DIPHENYLBORON BROMIDE.—Diphenylborinic anhydride in methylene chloride was added to boron tribromide in methylene chloride according to $3(\phi_2B)_2O+2BBr_3 \rightarrow 6\phi_2BBr+B_2O_3$ at −80°C. The solvent was removed at room temperature and the residue distilled twice. A fraction boiling at 112°/0·05 mm; lit.[7] b.p. 115°/0·05 mm, was identified as diphenylboron bromide, n_D^{20} = 1·6353; lit. n_D^{20} = 1·6346[7] or 1·6325[8] (found: Br, 32·5; calc. for $C_{12}H_{10}BBr$; Br, 32·7 %).

TRICYCLOHEXYLBORON.—Triethylamine borane (Et_3NBH_3) was synthesized[9] by mixing anhydrous triethylamine hydrochloride (1 mole) with sodium borohydride (1 mole) in triethylamine solvent at −10°C. Water (1 mole) was added slowly to the mixture. Sodium chloride was filtered off and the borane separated from ethylamine by distillation. Triethylamine borane (1 mole) was heated under an atmosphere of nitrogen to 100-120°, and cyclohexane (3 mole) was added dropwise. The reaction mixture was refluxed for a further 5-6 h and the liberated amine distilled off. White crystalline tricyclohexylboron was purified by distillation and sublimation; b.p. 131-2°/2 mm, m.p. 118°; lit.[10] b.p. 130-1°/2 mm, m.p. 118°[11] (found: B, 4·4; calc for $C_{18}H_{33}B$: B, 4·2 %). A further sample was purified by crystallization from freshly-distilled 1,4-dioxan. The infra-red spectrum showed no absorption attributable to B—O stretch in the 1300 cm^{-1} region. The compound smoulders in dry air and was handled in an oxygen-free atmosphere.

ENTHALPIES OF TRANSITION

Two methods were used: (A) a static method consisting of an all-glass vapour tensimeter incorporating a spiral gauge (Springham). The accuracy of the system was checked using water and from a $\log_{10}P$ (mm) against $1/T$(°K) plot the following vapour pressures at 10, 20, 30 and 40°C were obtained, (literature data[12] in parentheses); 9·23 (9·203), 17·38 (17·529), 31·62 (31·824) and 55·21 (55·338) mm. (B) A dynamic distillation technique, establishing an equilibrium between liquid and vapour, and stabilizing the pressure with a Cartesian manostat. This system was checked with propionic acid,[13] and the average deviation of eight observations over 63-111°C was ±2 %.

The experimental data obtained and reported in table 1 are represented in the form,

$$\log_{10}P\,(\text{mm}) = a - b/T\,(^\circ\text{K}),$$

where *a* and *b* are obtained from a least-squares analysis.

TABLE 1

compound	range (°C)	*a*	$10^{-3}b$(°K)	ΔH (liq.→g) (kcal mole^{-1})	method
ϕBCl_2	0-45	6·29	1·76	8·05±0·2	A
ϕ_2BCl	90-212	6·48	2·17	9·9±0·5*	B
ϕBBr_2	118-160	7·63	2·30	10·5±0·5*	B
ϕ_2BBr	163-243	8·35	3·15	14·4±0·5*	B
ϕ_3B	150-295	8·28	3·36	15·4±0·5*	B

*an error of ±0·5 kcal was assigned to these data as the experimental ranges do not include 25°C.

ERRORS.—In contrast to the procedure[14] we adopt the following procedure: (i) for less than five observations, the error is taken as the range; (ii) for five or greater, the error is quoted as twice the standard deviation from a *single* observation. The net error is calculated as the root of the sum of the squares of the constituent errors.

CALORIMETER

The calorimeter was a constant-temperature-environment type fully immersed in a thermostat controlled to 25·0±0·01°C.[15] The precision and accuracy were checked by two standard reactions, one exothermic and the other endothermic. For the enthalpy of neutralization of tris-(hydroxymethyl)-aminomethane in excess 0·1M HCl, the mean of five determinations was −7·174±0·02 at 25°C and *N* = 730 (lit.,[16] 7·104 kcal mole^{-1} at 25°C and $N = 1330$). The dilution enthalpy for THAM is small. For the integral enthalpy of solution of potassium chloride in water, $\Delta H = 4{\cdot}212 \pm 0{\cdot}008$ kcal mole^{-1}, at 25°C and $N = 200$ (lit.,[17] 4·206 kcal mole^{-1} at 25°C and $N = 200$). Enthalpies are quoted in units of 1 cal. = 4·1840 abs. J, and were measured at 25·0 ± 0·1°C except where stated otherwise.

FINAL THERMODYNAMIC STATE

PHENYLBORON HALIDES.—These compounds hydrolyze quantitatively to phenylboronic acid and hydrogen halide. The quantities of phenylboron halides were selected such that the phenylboronic acid remained in solution.

DIPHENYLBORON HALIDES.—Hydrolysis is quantitative also but phenylborinic acid is an intractable compound [18] with a small aqueous solubility and decomposes slowly on standing. Hydrolyses were performed therefore in saturated solutions of phenylborinic acid. It was assumed that the thermal effect due to further dissolution (or precipitation) as the reaction proceeded was negligible. Using this technique, the diphenylborinic acid product can be assumed to form in its standard state. In independent experiments the slow decomposition of diphenylborinic acid was not thermally detectable. Both ϕBBr_2 and ϕ_2BCl have m.p. close to 25°C. Liquid ϕ_2BCl could be supercooled to 25°C so the thermodynamic data for this compound apply to the metastable liquid at 25°C. Phenylboron dibromide did not supercool and hence was studied in the liquid state at 30°C. It was assumed that the difference in ΔH_{obs} at 25 and 30° was within the limits of error so these data apply to the hypothetical liquid state at 25°C. The assumption is probably justified as an isolated observation of ΔH_{obs} (30°C) for ϕ_2BCl was only marginally different from the observations at 25°.

TRIPHENYLBORON AND TRICYCLOHEXYLBORON.—A basic oxidizing medium [1] consisting of 0·1 M sodium hydroxide in aqueous 0·1 M hydrogen peroxide was used. Oxidative hydrolysis thus yielded phenol (or cyclohexanol) and boric acid quantitatively. Independent experiments showed the base-catalyzed decomposition of hydrogen peroxide was not thermally detectable. Preliminary experiments with these compounds were unsuccessful in that, following ampoule fracture the compound floated and hydrolysis continued over periods of 30 min or more. In subsequent experiments, the compounds were dissolved in a known amount of 1,4-dioxan for triphenylboron and cyclohexanol for tricyclohexylboron. Both solvents were distilled (dioxan from sodium) immediately prior to use. Hydrolyses were then complete within a few minutes. This technique necessitated the determination of the enthalpies of solution of (i) 1,4-dioxan in the basic oxidizing medium, (ii) cyclohexanol in the basic oxidizing medium, (iii) triphenylboron in 1,4-dioxan, and (iv) tricyclohexylboron in cyclohexanol.

TABLE 2

compound	n	ΔH_{obs} (Cl) kcal mole^{-1}
ϕBCl_2	2360	−40·7 (25°C)
	2425	−40·5
	2743	−40·0
	4320	−40·6
	3620	−40·1
	3300	−40·1
	2914	−40·2
		ΔH_{obs}(Br)
ϕBBr_2	3524	−48·6 (30°C)
	4603	−48·8
	4002	−48·7
	7010	−49·0
	4257	−49·0
	5350	−49·0

ΔH_f° ϕBCl_2(liq) ; 25°C = −71·7 ± 0·6 kcal mole^{-1}

ΔH_f ϕBBr_2(liq) ; 25°C = −41·4 ± 0·6 kcal mole^{-1}

RESULTS

PHENYLBORON HALIDES

These compounds hydrolyze rapidly but without undue violence according to

$$\phi BX_2(\text{liq})+(n+2)H_2O(\text{liq}) = [\phi B(OH)_2+2HX]nH_2O, \quad \Delta H_{\text{obs}}(X),$$

where X = Br, Cl. Hence

$$\Delta H_f^\circ[\phi BX_2, \text{liq}] = \Delta H_f^\circ[\phi B(OH)_2, aq]+2\Delta H_f^\circ HX,\left[\frac{n}{2}H_2O\right]- 2\Delta H_f^\circ[H_2O, \text{liq}]-\Delta H_{\text{obs}}(X).$$

DIPHENYLBORON HALIDES

These compounds hydrolyse rapidly but without undue violence in saturated aqueous diphenylborinic acid. The standard state (s.s.) of this latter compound is ambiguous.

$$\phi_2BX(\text{liq})+(n+1)H_2O(\text{liq}) = \phi_2B(OH)(\text{s.s})+HXnH_2O$$

from which

$$\Delta H_f^\circ[\phi_2BX, \text{liq}] = \Delta H_f^\circ[\phi_2BOH(\text{s.s.})]+\Delta H_f^\circ[HX, nH_2O]- \Delta H_f^\circ[H_2O, \text{liq}]-\Delta H_{\text{obs}}(X).$$

TABLE 3

compound	n	ΔH_{obs} (Cl) kcal mole^{-1}
ϕ_2BCl	1644	−16·9*
	2018	−17·3
	1433	−17·1$_5$
	2054	−17·4
	2612	−17·4
	1921	−17·0
		ΔH_{obs}(Br)
ϕ_2BBr	1590	−22·5
	1758	−22·5
	1677	−21·9
	1565	−22·1$_5$
	1775	−22·1$_5$
	1870	−21·5
	1616	−21·6
	1824	−21·9

* at 30°C

$$\Delta H_f[\phi_2BCl, \text{liq}]-\Delta H_f^\circ[\phi_2BOH(\text{s.s.})] = 45{\cdot}5\pm0{\cdot}18 \text{ kcal mole}^{-1}.$$
$$\Delta H_f^\circ[\phi_2BBr, \text{liq})-\Delta H_f^\circ[\phi_2BOH(\text{s.s.})] = 61{\cdot}3\pm0{\cdot}38 \text{ kcal mole}^{-1}.$$

Incorporating the approximate figure,[1] $\Delta H_f^\circ[\phi_2BOH, (\text{s.s.})]\sim -78$ kcal mole^{-1}, then $\Delta H_f[\phi_2BCl,\text{liq}]\sim -32$ and $\Delta H_f^0[\phi_2BBr,\text{liq}]\sim -17$ kcal mole^{-1}.

TRIPHENYLBORON

This was oxidatively hydrolysed as a dioxan solution in a mixture of aqueous 0·1 M hydrogen peroxide and 0·1 M sodium hydroxide (a.e.b. = aqueous excess base).

$$\phi_3B \text{ (dioxan soln)}+3H_2O_2(\text{a.e.b.}) = [3\phi OH+H_3BO_3] \text{ (a.e.b.)/dioxan}, \qquad \Delta H_{\text{obs}}$$

The following ancillary data were also determined:

$$\phi_3\text{B (cryst.)} + \text{dioxan} = \phi_3\text{B (dioxan soln)}, \qquad \Delta H_3$$

and

$$\text{dioxan (liq)} + \text{a.e.b.} = \text{dioxan/(a.e.b.)}, \qquad \Delta H_1.$$

Hence

$$\Delta H_f^\circ \phi_3\text{B(c)} = \Delta H_f[\phi_3\text{B, dioxan soln}] - \Delta H_3 = 3\Delta H_f[\phi\text{OH(a.e.b.)}] + \Delta H_f[\text{H}_3\text{BO}_3\text{(a.e.b.)}] - 3\Delta H_f[\text{H}_2\text{O}_2\text{(a.e.b.)}] - \Delta H_{\text{obs}} - \Delta H_3 + (N_1/N_2)\Delta H_1,$$

where N_1 and N_2 are the number of moles of dioxan and triphenylboron respectively. The enthalpy of solution of ϕ_3B in a non-polar solvent (benzene) was also measured to obtain an estimate of the enthalpy of fusion of ϕ_3B.

TABLE 4

reaction	n(dioxan, ϕ_3B)	ΔH_3[kcal mole^{-1}]
ϕ_3B in 1,4-dioxan	654	3·2
	740	3·4
	795	3·3
	849	3·1
	632	$3{\cdot}3_5$

	n(dioxan, H$_2$O)	ΔH_1
1,4-dioxan in a.e.b.	310	−2·27
	317	−2·29
	332	−2·28
	409	−2·27

	n(benzene, ϕ_3B)	ΔH(soln)
ϕ_3B in benzene	628	4·1
	562	3·8
	550	4·2
	427	4·2
	533	3·9
	450	4·2

	10^2N_1	10^4N_2	ΔH_{obs} (kcal mole^{-1} of ϕ_3B)	$[\Delta H_{\text{obs}} - N_1\Delta H_1/N_2]$
ϕ_3B (dioxan soln) in a.e.b.	1·552	3·9010	−376·3	−276·6
	1·479	2·4837	−410·2	−274·4
	1·899	4·1719	−381·2	−277·4
	2·052	4·5474	−381·5	−278·6
	1·184	4·2442	−340·5	−276·9
	1·249	4·7270	−333·5	−273·3
	1·578	4·7852	−351·0	−275·8

$$\Delta H_{\text{soln}}\ (\phi_3\text{B in dioxan}) = \Delta H_3 = 3{\cdot}3 \pm 0{\cdot}13 \text{ kcal mole}^{-1}.$$

$$\Delta H_{\text{soln}}\ (\phi_3\text{B in benzene}) = 4{\cdot}1 \pm 0{\cdot}2 \text{ kcal mole}^{-1}.$$

$$\Delta H_{\text{soln}}\ (\text{dioxan in a.e.b.}) = \Delta H_1 = -2{\cdot}28 \pm 0{\cdot}01 \text{ kcal mole}^{-1}.$$

$$\Delta H_f^\circ(\phi_3\text{B, cryst.});\ 25^\circ\text{C} = 11{\cdot}6 \pm 1{\cdot}9 \text{ kcal mole}^{-1}.$$

TRICYCLOHEXYLBORON

This compound was oxidatively hydrolyzed as a cyclohexanol solution in the basic oxidizing medium.

$$(\text{C}_6\text{H}_{11})_3\text{B (cyclohexanol soln)} + 3\text{H}_2\text{O}_2\ \text{(a.e.b.)} = [3\text{C}_6\text{H}_{11}\text{OH} + \text{H}_3\text{BO}_3]\ \text{(a.e.b.)/cyclohexanol}, \qquad \Delta H_{\text{obs}}$$

The following ancillary data were determined:

$$(C_6H_{11})_3B\ (\text{cryst}) + \text{cyclohexanol} = (C_6H_{11})_3B\ (\text{cyclohexanol soln}), \qquad \Delta H_3$$

and

$$\text{cyclohexanol(liq)} + \text{a.e.b.} = \text{cyclohexanol/(a.e.b.)}, \qquad \Delta H_1.$$

Hence

$$\begin{aligned}\Delta H_f^\circ[(C_6H_{11})_3B, \text{cryst}] &= \Delta H_f[(C_6H_{11})_3B, \text{cyclohexanol}] - \Delta H_3\\ &= 3\Delta H_f[C_6H_{11}OH(\text{a.e.b.})] + \Delta H_f[H_3BO_3(\text{a.e.b.})] - 3\Delta H_f[H_2O_2(\text{a.e.b.})] +\\ &\qquad N_1\Delta H_1/N_2 - \Delta H_{\text{obs}} - \Delta H_3,\end{aligned}$$

where N_1 and N_2 are the number of moles of cyclohexanol solvent and tricyclohexylboron respectively.

TABLE 5

reaction		n (cyclohexanol : $(C_6H_{11})_3B$)	ΔH_3, kcal mole^{-1}	
$(C_6H_{11})_3B$ in cyclohexanol		955	1·9	
		$n(H_2O$, cyclohexanol)	ΔH_1	
cyclohexanol in a.e.b.		313	−1·97	
		285	−1·93	
		296	−1·97	
		350	−2·01	
		266	−2·00	
	10^2N_1	10^4N_2	ΔH_{obs} (kcal mole^{-1} of $(C_6H_{11})_3B$)	$[\Delta H_{\text{obs}} - N_1\Delta H_1/N_2]$
$(C_6H_{11})_3B$ (cyclohexanol soln) in a.e.b.	3·2278	3·1851	−470·3	−269·7
	2·7941	3·9304	−415·7	$-274{\cdot}9_5$
	2·7221	4·3454	−399·3	−275·3
	2·8519	4·7258	−394·4	−274·9
	3·2218	3·9266	−432·7	−270·2
	2·6420	3·5962	−415·7	−270·2
	2·3224	3·2005	−416·8	−273·1

$$\Delta H_{\text{soln}}\,[(C_6H_{11})_3B \text{ in cyclohexanol}]\ 25°C = \Delta H_3 = 1{\cdot}9 \pm 0{\cdot}3^*\ \text{kcal mole}^{-1}.$$
$$\Delta H_{\text{soln}}\,(\text{cyclohexanol in a.e.b.})\ 25°C = \Delta H_1 = -1{\cdot}98 \pm {\cdot}03\ \text{kcal mole}^{-1}.$$
$$\Delta H_f^\circ[(C_6H_{11})_3B, \text{cryst}];\ 25°C = -115{\cdot}3 \pm 2{\cdot}5\ \text{kcal mole}^{-1}.$$

* estimated error

ANCILLARY DATA AND CALCULATIONS

The enthalpies of mixing of the products of each hydrolysis were ignored as was the enthalpy of dilution of ϕ_3B in dioxan and $(C_6H_{11})_3B$ in cyclohexanol. The ancillary data used for the ϕ_3B calculation have been reported.[1]

In addition, we have used:

$$\Delta H_f^\circ[\phi B(OH)_2,c]^1 = -172{\cdot}0 \pm 0{\cdot}5,\ \Delta H_f^\circ[\phi B(OH)_2,\ aq]^1 = -168{\cdot}8 \pm 0{\cdot}5,\ \Delta H_f^\circ[\text{HCl } 3000\ H_2O]^{19} = -39{\cdot}96,\ \Delta H_f^\circ[\text{HBr } 3000\ H_2O]^{19} = -29{\cdot}05 \pm 0{\cdot}09,\ \Delta H_f^\circ[C_6H_{11}OH,\ \text{liq}]^{20} = -83{\cdot}45\ \text{kcal mole}^{-1}.$$

The enthalpies of dilution of HBr and HCl were taken from ref. (21). Combining the data of tables 1-4 we summarize in table 6.

TABLE 6

	ϕBCl_2	$\phi_2 BCl$	ϕBBr_2	$\phi_2 BBr$	$\phi_3 B$	$(C_6H_{11})_3B$
ΔH_f°(c), 25°C	—	—	—	—	$11{\cdot}6 \pm 1{\cdot}9$	$-115{\cdot}3 \pm 2{\cdot}5$
ΔH_f°(liq), 25°C	$-71{\cdot}7 \pm {\cdot}6$	*ca.* −32	$-41{\cdot}4 \pm {\cdot}6$	*ca.* −17	—	—
ΔH_f°(g), 25°C	$-63{\cdot}6 \pm {\cdot}6$	*ca.* −22	$-30{\cdot}9 \pm {\cdot}7$	*ca.* −3	$31{\cdot}1 \pm 2{\cdot}0$*	$-95{\cdot}8 \pm 2{\cdot}7$ †

* taking $\Delta H(c \rightarrow g) = \Delta H_s(\phi_3B \text{ in } \phi H) + \Delta H(\text{liq} \rightarrow g)$.

† assuming $\Delta H(c \rightarrow g, \phi_3B) = \Delta H(c \rightarrow g, (C_6H_{11})_3B)$; the error was doubled for tricyclohexylboron.

DISCUSSION

BOND ENERGIES AND MOLECULAR STRUCTURE

Calculation of the boron-carbon bond energy in the above compounds requires a knowledge of $\Delta H_f^\circ \phi(g)$, which may be derived from $\Delta H_f^\circ \phi(g) = D(\phi{-}H) - \Delta H_f^\circ H(g) + \Delta H_f^\circ \phi H(g)$. The standard enthalpies of formation of atomic hydrogen and benzene gas are accurately known but the bond dissociation energy of phenyl-hydrogen varies greatly, e.g. some data (in eV), obtained by several different methods, are 4·42,[22] 4·64,[23] 4·58,[24] 4·52,[25] and 4·47.[25]

We have used the mean of these data ($104{\cdot}4 \pm 1{\cdot}7$ kcal) and an error of four times the standard deviation. This gives $\Delta H_f^\circ \phi(g) = 72{\cdot}1 \pm 1{\cdot}7$ kcal mole^{-1} and is in agreement with a " best " value selected recently,[26] from which we also select $\Delta H_f^\circ C_6H_{11}(g) = 12 \pm 3$ kcal mole^{-1}. Using these figures and the data in table 6 we tabulate the boron-carbon bond energy. The following ancillary data were used:

$\Delta H_f^\circ H(g)^{27} = 52{\cdot}1$, $\Delta H_f^\circ \phi H(g)^{28} = 19{\cdot}82$, $\Delta H_f^\circ B(g)^{27} = 132{\cdot}8 \pm 4{\cdot}0$,
$\Delta H_f^\circ Br(g)^{27} = 26{\cdot}74$, $\Delta H_f^\circ Cl(g)^{27} = 28{\cdot}94$ kcal mole^{-1}.

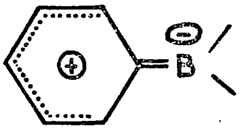
We further assume the boron-halogen bond energies in arylboron halides are equal to those in the boron trihalides (using data from ref. (27): E(B—F) = 153·2, E(B—Cl) = 105·3, E(B—Br) = 87·3, all ±1·3 kcal).

TABLE 7

	ϕBCl_2	$\phi_2 BCl$	ϕBBr_2	$\phi_2 BBr$	$\phi_3 B$	$(C_6H_{11})_3B$
E(B—C)	$115{\cdot}8 \pm 2{\cdot}3$	*ca.* 112	$114{\cdot}7 \pm 2{\cdot}3$	*ca.* 110	$106{\cdot}0 \pm 2{\cdot}3$	$88{\cdot}2 \pm 3{\cdot}4$
$E(B{-}C)_\pi^*$	28	24	27	22	18	—

* see text.

A feature of these data is the wide divergence of the boron-carbon (aliphatic) bond energy from the boron-carbon (aromatic) bond energy; this is not an uncommon feature of organometallic systems (see fig. 1). For organo-boron systems the enhancement may be due to resonance stabilization, i.e., contribution from



Strong support for this idea comes from molecular dipole moments [30] and various spectroscopic and chemical evidence.[31] However, some chemical evidence [32] implies the opposite. Our estimate of the magnitude of this contribution falls between two other estimates. Lockhart [33, 34] estimates the barrier to boron-phenyl rotation in ϕBCl_2(C_{2v} planar) from a knowledge of torsional modes and the reduced moment as ~45 kcal, and that in ϕBBr_2 (probably C_{2v} planar) as ~37 kcal. Taking 88 kcal as the σ-contribution to the E(B—C) bond energy, we obtain $E(\text{B—C})_{\pi}$ as 28 and 27 for these molecules. A simple Hückel molecular orbital (HMO) treatment [35] of several triarylborons indicates the resonance stabilization for a coplanar system to be 12 kcal, i.e., ~4 kcal per boron phenyl bond. In a molecule such as tetraphenyltin, where the enhancement is ~15 kcal per carbon-tin bond it is difficult to see how resonance would contribute to stabilization as the tin is tetrahedrally coordinated. Hence, it is also possible that the bond strength enhancement in boron aryls relative to boron alkyls is a σ-bond effect or even a combination of the two effects (the enhancement in organoboron systems is considerably larger than in the other cases).

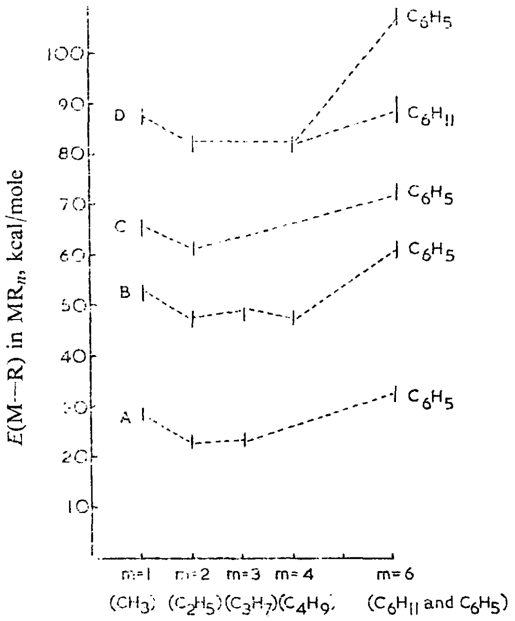


FIG. 1.—Variation in bond energy (E(M—R) in MR$_n$) with number of carbon atoms in R(m). Points A are where M is mercury, points B where M is tin, points C where M is phosphorus, and points D where M is boron.

From the data in table 7, the boron-phenyl bond decreases in strength with successive phenyl substitution. Phenylboron dichloride (and, by analogy, phenylboron dibromide) is planar by electron diffraction. In this configuration, resonance stabilization is a maximum. The difference between ϕBCl_2 and ϕBBr_2 is not significant. This is in line with Perkins' observations,[36] who investigated the π-electronic structures of these molecules by a molecular orbital-self consistent field technique, that the bond order of B—C in ϕBBr_2 and ϕBCl_2 is about the same. In the diphenyl compounds, the phenyl rings are twisted out of the BC_2X plane to reduce ring-ring steric interaction at the expense of resonance stabilization. Weismann [35] *et al.* estimate the net potential energy of several triaryl borons, assuming a rigid σ-skeleton, by summing non-bonded interactions (from an exponential-six function) and the resonance energy (from an HMO treatment). They express the net potential energy as a function of the angle $(90-\tau)$ of twist of the phenyl group from the BC_3 plane. For tri-phtolyl boron, and other more hindered molecules, they deduce an equilibrium configuration with $\tau \sim 45°$, when the resonance contribution (proportional to sin τ) has decreased ~ 30 % from its maximum value. Assuming triphenylboron has the same configuration, then 10 kcal ($E(B—C)_{\pi}$ in $\phi BCl_2 - E(B—C)_{\pi}$ in ϕ_3B) represents a 30 % decrease in resonance stabilization giving a total resonance energy of ~ 33 kcal per bond. This is slightly larger than that observed (~ 28 kcal).

It has been tacitly assumed that the boron-halogen bond strength remains constant in ϕBX_2 and ϕ_2BX and that the observed variation in $E(B—C)$ is due to the influence of the phenyl groups. This is probably justified, as the B—Cl bond length varies little with environment [37] (e.g., in BCl_3, $1{\cdot}73 \pm {\cdot}02$ Å; in ϕBCl_2, $1{\cdot}72 \pm {\cdot}03$ Å). There are no corresponding data for the bromo-derivatives.

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