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Declaration

The work described in this thesis was carried out in the University of Durham between October 1988 and September 1991. It has not been submitted, either completely or in part, for another degree in this or any other University, and is the original work of the author except where acknowledged by reference.

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Alkoxy and Related Derivatives of Main Group Elements

ABSTRACT

A series of derivatives of the brominated alcohol 3-bromo-2,2-bis(bromomethyl)-1-propanol were prepared with a view to eventual use of such derivatives as flame retardants. The derivatives took the form of alkoxide compounds of main group elements, except for a few compounds of non-main group elements, which were added for their known application in the flame retardant field. Many of these derivatives were liquids at room temperature, so were of limited use for flame retarding polymers etc., but were of interest due to the trends shown in their spectra.

Of the solid derivatives, the fully substituted monomeric boron and silicon compounds were tested by high temperature DSC & TGA techniques. The silicon derivative showed potential for application in ABS-type polymers, and would be worthy of further study. The simple orthoborate did not perform as well. The other solid species produced were tested by DSC to 400°C and the results reviewed.

Derivatives of the brominated diol 2,2-bis(bromomethyl)-1,3-propanediol were also prepared, with the same aim.

Some reactions of tetrahydroborate with 1,2-dihydroxybenzene or sulphur were studied. The spirocyclic bisdiol borate anion was successfully prepared via this route, although the target of the monodioldihydro species was not formed. The reactions with sulphur were aimed at producing an active borane-type species, but were also of interest for the structural problems they raised. No definite conclusions were reached regarding the product of these reactions, however.

Some work was also performed on a novel route to carboranes by reacting a carbene with a borane anion. The preliminary reactions did not indicate the presence of any carborane species.

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CHAPTER ONE

1 Introduction

1.1 The History of Flame Retardants

Since the dawn of time Man has been threatened by the very thing which gave him his ascendancy: fire. It brought him the means to defend himself and enabled him to move from using implements of stone to bronze and iron tools. At the same time, however, it was a menace which consumed his artefacts and all his constructions of wood, and history contains many examples of fire having a great effect on its course; the destruction of Jericho[1] and the great fire of London are just two examples.

So, because wood was such an important building material and was so susceptible to burning, attempts were made to protect the timber to some extent from the threat. One can only presume that such attempts had been made for as long as the threat existed, for there are references to it in the earliest literature. Αινειου (Aineias) in his Πολιορκητικα (Poliorketica - A Tactical Treatise on How to Survive Under Siege) includes a section entitled "Materials for quenching fires", in which he recommends the use of vinegar, which will also "make it hard to set alight again". "Better still", he continues, "smear it beforehand with birdlime; for this is fireproof."[2,3] At the siege of Piraeus in 85 B.C., it is recorded that the siege towers were treated with a solution of alum to protect them against being set alight by the defenders. There are references to the protection against fire used as a weapon, but equally deadly was accidental fire in the increasing number of buildings, and the use of woven textiles, which in time came to dominate the flame retardant scene. An early such reference was by one Sabattini, a gentleman of the Italian theatre, who in 1638 suggested that clay be added to paint for use in theatres to prevent the scenery from catching fire. The first patent for a flame retardant was granted very early in patent history to Obadiah Wyld. In 1735 he patented a mixture of alum, ferrous sulphate and borax for use on cotton[4]. In the nineteenth century, Gay-Lussac followed with the first systematic study of the subject using the materials available to him at the time. He found that ammonium chloride, sulphate and phosphate were effective on their own, and also sometimes as a mixture with borax. These he applied to linen and jute fabrics[5]. However, these mixtures had the disadvantage that they were relatively easily washed out of the fabric, and it was not until the early twentieth century that W.H. Perkin developed the first real "washproof" flame retardant for textiles by precipitating insoluble tin oxide *within* the fibres[6]. However, washfastness remains a problem for textile flame retardants to this day.

1.2 The Need for Flame Retardants

As has been introduced above, wood and various natural textiles such as cotton, linen and jute, were the first applications of flame retardants. These substances are mainly natural cellulose polymer, and as modern synthetic polymers were developed, particularly since the Second World War, the problem of making such systems flame retardant has produced a multitude of methods for achieving this, which is necessary because of the flammability of many of these polymers. Wood is still used as the major fuel in many parts of the world, thus deriving energy from the burning of cellulose, which has quite a small heat of combustion (19 kJ/g for cotton).

Many modern polymers have far higher heats of combustion, some even reaching the levels associated with well known fuels. The table below gives some representative values for some common materials:

Material	Heat of combustion (kJ/g)	LOI*
PVC	18	0.42
Cotton	19	0.18
PET	22	0.21
Wool	27	0.25
Ethanol	30	-
Nylon-6	39	0.21
Polystyrene	42	0.19
Polypropylene	47	0.19
Polythene	47	0.18
Propane	51	-
Methane	56	-

Source: Chem. in Brit., 1987, March, p.235; D. Price, A.R. Horrocks & M. Tunc. Also J. Soc. Dyers Colour, 1983, 99, 191; A.R. Horrocks.

* LOI - Limiting Oxygen Index (see text below).

It can be seen from this limited example that many of the most common polymers in use today, e.g. polythene, polystyrene, have heats of combustion comparable with materials which are used as fuels, thus posing a considerable risk if they ever catch fire, as the greater is the heat of combustion, the more heat is available to volatilise the polymer, the faster the fire can spread, and thus the more damage it can do. The

LOI value in the table is the Limiting Oxygen Index, and represents the minimum mole fraction of oxygen in the gas surrounding the polymer which will support continued combustion. Clearly, any value below 0.21 means that the material will continue to burn even in conditions where there is a deficiency of oxygen, such as those found in many fires, so wool and PVC will not normally continue to burn unaided in air (though it must be remembered that plasticised PVC contains up to 50% by weight of flammable plasticiser). In such conditions, it is highly likely that incomplete combustion will take place, often producing highly toxic products[7]. Again, the values for polymers such as polythene and polystyrene are below this threshold level.

1.3 Recent Developments

Modern polymers, then, pose a major fire risk due to their high heats of combustion and low LOI values. However, when compared to such materials as ethanol, they are obviously much less volatile, and will thus have much higher flash points and lower flammabilities. The physical state of the polymer is very important in this regard, however, and woven polymer fibres in textiles are particularly at risk. Also, expanded foams can be dangerous due to the large surface area of polymer which is presented, though this risk can be reduced by blowing the foams with an inert gas such as carbon dioxide. These risks have led to a large increase in work on flame retardant systems in the last fifty or so years.

The very early flame retardants, as noted above, were fairly simple, readily available, non-flammable materials which were simply coated onto the surface of the flammable material, be it wood or cloth, or mixed with it in the case of paint. This situation continued for many years, and these techniques are still used today to some extent. However, there was the recurring problem of getting the flame retardant to remain where it was needed, i.e. on the material it was supposed to be protecting. This was first tackled by Perkin with his wash-fast treatment of fabrics, but the major method of flame retardant incorporation in use today was developed along with modern synthetic polymers; this is melt blending. Many plastic articles are moulded into shape using molten polymer, and fibres are spun from either the melt or a solution. These methods offer a means of adding various compounds to the polymer to yield a homogeneous end product. The additives can be blended as granules in the solid state, or compounded in the melt, or both[8]. Problems with this method lie in the temperatures at which it is carried out. Polymers are melt-processed at temperatures from 180°C to over 300°C in some cases, and towards the top end of this range many flame retardant materials decompose and thus lose their effectiveness in the finished product. Often a balance has to be struck between using the best compound for the job and one which is not as good but survives the processing better.

In the 1930's and '40's, when many of the first synthetic linear polymers were being invented and developed, it was found that organic compounds containing halogen were much more difficult to burn than ordinary hydrocarbons. This is exemplified by PVC, which contains only carbon, hydrogen and chlorine, has an LOI of 0.42, and is thus extremely difficult to burn, as well as having a low heat of combustion of 18 kJ/mol. Incorporation of organic halogen compounds into flammable polymers containing large amounts of hydrogen was found to make the whole system harder to burn. However, it was also found that quite large amounts of such compounds were needed to impart the desired flame retardancy; up to 20% by weight of additive[9]. This tended to have very undesirable effects on the very properties of the polymer for which it was being used in the first place. One way to reduce the amount of additive needed was to increase the percentage by weight of halogen in the additive, as flame retardant effect is often linearly related to the amount of halogen present[10]. The effectiveness also varies from halogen to halogen, bromine being the most effective[11], so brominated compounds are widely used, along with chlorinated species.

1.4 Synergy

However, the best way of reducing the loading of additive needed in a polymer to impart satisfactory flame retardance was discovered in the 1930's, when it was found that mixing antimony oxide with an organic halogen compound vastly reduced the amount of the latter required for the desired effect[12]. This is because the antimony and halogen interact synergistically, producing a greater combined effect than the sum of their individual effects. This discovery opened up a whole new area for flame retardants, enabling a much greater variety of systems to be used.

Work since then has been aimed at producing new systems, but using the same principles outlined above, so many commercial flame retardants today are halogenated organic species acting with some form of inorganic synergist. There are, however, other ways of incorporating the halogen into the polymer rather than it being contained in an additive. One is to halogenate the backbone of the polymer after formation, and then only the synergist needs to be added, such as is sometimes done with polythene[9]. Another way is to introduce the halogen into the backbone of the polymer reactively, by means of a halogenated monomer. This can be introduced as a mixture with the ordinary monomer, or block copolymers can be formed from ordinary and halogenated monomers. This "reactive" method of flame retardant incorporation often requires the complete redesigning of a polymer, so it is being increasingly used as new fire regulations are introduced. A few decades ago, polymers were introduced with little concern for their flammability, and flame retardant additives were used to make them conform to regulations as these steadily became stricter. Nowadays, however, it is often more effective in the long run to have flame retardance as a fundamental consideration from the outset of the development of a new polymer system.

1.5 Modes of Action

So it can be seen that polymers, both natural and synthetic, have increasing need for the use of flame retardants, mainly due to the ever stricter fire regulations which are continually being introduced. These flame retardants can be incorporated in several ways: as surface coatings, blended with the fluid polymer, or included in the structure of the polymer itself, and they consist of a varied list of materials, from simple metal oxides to reactive halogenated monomers. But how do they work?

The modes of action of flame retardants cover a wide range of chemical and physical processes, and by no means all of them are fully understood. Some of the simplest mechanisms are those of flame retardants applied as coatings onto textiles and wood. Antimony oxide on cellulose reacts endothermically with the hydroxyl groups on the surface of the polymer, thus absorbing some of the heat necessary for flame propagation, and forming non-flammable products which also shield the underlying material from the heat, preventing its degradation into volatile fuel components. Other species melt when heated to form an impervious, glassy layer on the surface of the polymer, insulating the underlying material. This also has the effect of preventing any volatiles escaping and igniting . Some of these coatings, such as borax, also decompose on heating to give gases, in this case water, which cool the flame and help to quench it. Other systems which act in a similar way include carbonates (carbon dioxide), ammonium salts (ammonia) and aluminium hydroxide (water). The latter species also yields aluminium oxide which is an excellent thermal conductor, and serves to remove heat from the flame zone extremely quickly, helping to reduce the rate at which the polymer is pyrolysed and fuel produced.

Another method to reduce fuel production is to alter the chemistry of the decomposition pathway of the polymer so that instead of breaking up to form small, volatile, flammable organic molecules, it loses species such as water and the carbon is retained as char, which is very difficult to ignite. Certain acidic phosphorus compounds act this way in cellulosic materials by inhibiting the production of laevoglucosan (which decomposes to organic volatiles), and promoting dehydration of the polymer[13]. Phosphorus compounds in polystyrene, on the other hand, serve to catalyse the scission of the molten polymer chain, thereby reducing its viscosity and helping it to flow away from the flame[14]. It has been suggested that halogens in polymers can act by increasing the heat capacity of the system, thereby increasing the heat input required to volatilise a given mass of polymer, while at the same time reducing the fuel content of the polymer and so reducing the heat evolved on burning the given mass[15]. However, the main function of halogens is thought to be in the flame itself after the halogen containing flame retardant has decomposed[16].

Burning is essentially a free radical chain reaction. Polymers, as solids, do not burn, but their decomposition products do. An external heat flux is required to raise the temperature of the polymer surface to its degradation point. Chain scission then occurs, and small, volatile pyrolysis products are released. if these are flammable, the external heat source may cause them to catch fire, thus increasing the heat flux to the polymer surface and increasing the rate of fuel formation. Eventually, the rate may increase to such a level that the heat flux due to the burning degradation products is sufficient to produce enough fuel to make the flame self-sustaining, removing the need for an external heat source.

Within the flame, the fuels break down into free radicals in a highly complex, highly exothermic series of reactions which eventually produce water and carbon dioxide. The number of reactions involved is very high, but the key steps involve only a few major species, such as H• and OH•. The halogenated flame retardants are thought to interfere with the propagation of this chain reaction by trapping the small, chain propagating radicals to form products such as HBr or HOBr. These can then react further with propagating radicals, eventually forming stable, non-flammable products, such as water. The Br• radicals can then be re-formed to take part in a great many more quenching, radical trapping reactions before being dispersed by the flame. This mechanism acts to reduce the rate of energy production in the flame by removing the rate-limiting species, thereby reducing the amount of polymer pyrolysed to fuel to such an extent that the flame ceases to be self-sustaining and is extinguished.

As has been mentioned above, the use of Sb_2O_3 with halogenated compounds as flame retardants enables the amount of organohalogen species for a given effect to be drastically reduced, e.g. from around 20% w/w to 2% w/w in some cases, with the associated retention of the polymer's physical properties. The Sb_2O_3 and the halogenated material act synergistically, giving a greater joint effect than the sum of their individual effects, because they react together in a fire to produce species which are more efficient flame retardants than the original compounds. This has been shown by thermal analysis of halogenated flame retardants both alone and in combination with Sb_2O_3. Using the technique of thermogravimetric analysis (TGA), in which weight loss is measured as a function of temperature, it was found that on heating a chlorinated compound to 400°C, the weight loss corresponded to the loss of chlorine from the compound as HCl. On the addition of an equal weight of Sb_2O_3, the loss of weight indicated the formation of $SbCl_3$, which was also found by analysis of the gas evolved on heating[17]. This was presumably formed by the interaction of Sb_2O_3 with the HCl produced:

$$Sb_2O_3 + 6\,HCl \longrightarrow 2\,SbCl_3 + 3\,H_2O$$

A similar reaction could also produce antimony oxychloride:

$$Sb_2O_3 + 2\,HCl \longrightarrow 2SbOCl + H_2O$$

which can then break down to give $SbCl_3$ in a series of reactions which vary according to the temperature[18]:

$$5\ SbOCl \xrightarrow{\hspace{3cm}} Sb_4O_5Cl_2 + SbCl_3 \quad (245\text{-}80°C)$$

$$4\ SbOCl \xrightarrow{\hspace{3cm}} Sb_3O_4Cl + SbCl_3 \quad (410\text{-}75°C)$$

$$3\ Sb_3O_4Cl \xrightarrow{\hspace{3cm}} 4\ Sb_2O_3 + SbCl_3 \quad (475\text{-}565°C)$$

Study of chlorinated compounds which were known not to generate HCl directly on heating indicated that, when heated with Sb_2O_3, the major primary product was SbOCl which then decomposed to give $SbCl_3$ which acted as the flame retardant species[17,19].

Whilst still in the molten polymer, the SbX_3 (where X is a halogen) has a similar effect to phosphorus compounds in cellulose, in that it catalyses reactions which form a carbonaceous char, thereby inhibiting the formation of volatile fuel components[20]. Volatilisation of the SbX_3 into the flame causes it to decompose, releasing X• radicals and forming $SbX_n•$ $(n = 1\text{-}2)$ radicals. All of these species can interact with the chain propagating radicals in the flame, quenching it as outlined above. The stepwise decomposition of the SbX_3 also releases the active X• more slowly than the halogenated species would on its own, thereby increasing the time for which the quenching species are active in the flame. There is also evidence to suggest that antimony oxides react with the polymer to give water, which has the effect of cooling the flame and helping to quench it, similarly to the effect shown by, for example, $Al(OH)_3$, which decomposes to give water.

Flame retardants, then, work in two basic areas:

a) the condensed phase, i.e. the solid or, more often, the liquid polymer.

b) the vapour/plasma phase in the flame.

The mechanisms of action are numerous and vary widely from system to system, and even vary for a particular system depending on where and under what conditions it is used. However, the fundamental purpose common to all flame retardants, wherever and however they work, is

to retard the production and combustion of fuel,

whether it be by chemically interfering with the degradation of the polymer or preventing sufficient heat from reaching the surface of the polymer or preventing the escape of fuel once formed. All the mechanisms outlined above have this ultimate goal.

1.6 Areas of Application

The systems into which the flame retardants are incorporated also cover a wide range. The applications for the major flame retardant types are illustrated overleaf.

Flame Retardant Type	Application
Sb/halogen	Phenolics, epoxy resins, polyesters, styrenes, polyurethanes, polyolefins, polycarbonates.
P/halogen	Phenolics, celluloses, styrenes, rayon, polyesters, polyurethanes, polyolefins, acrylics.
P esters	Celluloses, epoxy resins, polyesters, polyurethanes.
Sb_2O_3	Celluloses, PVC.
Borates	Celluloses, PVC, polyesters.
Metal oxides	Cellulose, PVC, polyesters, styrenes.

1.7 Problems

It can be seen that the vast majority of flame retardants contain as their active constituents a main group element, such as antimony, boron, phosphorus, and/or a halogen, bromine or chlorine, and that the majority of flame retardant applications involve some sort of synergy, e.g. antimony or phosphorus with halogen. These materials undoubtedly make the modern world a much safer place, but they also present associated problems of their own. The major problems are listed below:

1) Leachability
2) Alteration of polymer properties
3) Thermal stability
4) Hydrolytic stability
5) Production of toxic decomposition products
6) Glow

Some of these have already been mentioned. A major problem with flame retardants in textiles is to make them washfast. Simple systems, such as boric acid/borax or phosphate salts, can be easily applied by treating the fabric with an aqueous solution of the materials and then drying it. This can even be done at home[21]. However, being water soluble, these materials can be easily removed by washing, so are most useful for large items that are infrequently washed, such as theatre curtains or upholstery. The flame retardant can be made more durable by Perkin's method of precipitating insoluble inorganic oxides with the flame retardant, but this has a larger effect on the properties of the fabric[22] The use of insoluble flame retardants, such as Sb_2O_3 and organohalogen, or phosphorus/nitrogen systems gives systems which can be durable for up to fifty washes, but again, such treatments tend to have an adverse effect on the fabric texture and colour[23].

The alteration of the polymer properties can be caused by the large amounts of flame retardant required for effectiveness. This is often a problem with halogenated additives, and can usually be minimised by the use of a suitable synergist. Changes can also be caused by the incorporation of the flame retardant species into the polymer itself as a reactive monomer. This may possibly introduce a point of weakness into the polymer chain, so the structure of such "active" flame retardants must be carefully chosen to match that of the polymer. In effect, incorporating a flame retardant in this way is designing a new polymer system, which can be a long and expensive business.

The thermal stability of flame retardants is of paramount importance and must be finely balanced. Many flame retardants work by decomposing in some way in a polymer and thus interfere with the breakdown of the polymer to produce fuel. However, if the flame retardant decomposes at too low a temperature, the active species will not be available when the polymer degrades and burns. On the other hand, too high a degradation temperature leads to the fire taking hold so that when the temperature is sufficient for the flame retardant to become active, it is of little use. Ideally, the decomposition of the flame retardant and the substrate polymer should be fairly closely matched so that the active species produced by the flame retardant are present during the polymer breakdown and possible combustion. Another factor to consider is the processing involved in polymer production. "Additive" flame retardants are usually added to a polymer in the melt to ensure homogeneous distribution. In the case of, for example, Acrylonitrile/Butadiene/Styrene (ABS) polymers, this processing is done at around 250°C, and the usual flame retardants are organobromine compounds, many of which are unstable at such temperatures. Aliphatic bromides, though more effective, decompose during processing, so the more stable aromatic compounds must be used, but at a higher loading, thus affecting the properties of the finished product more.

The hydrolytic stability of the flame retardant is of obvious importance, especially for materials intended for outdoor use. Materials which hydrolyse only very slowly on exposure to atmospheric moisture may be destroyed by prolonged exposure to rain, for instance. The main problems with stability occur with the phosphorus ester-type of flame retardants, which are widely used in textiles. For example, tris(2-chloroethyl) phosphate is fairly stable to hydrolysis, but less so than tris(1,3-dichloro-2-propyl) phosphate, which resists attack, even by aqueous base[24]. This is probably due to the increased steric bulk of the

2-propyl group over the ethyl, and thus offers a possible way to overcome such instability.

It is in the nature of flame retardants to decompose to give volatile products, which raises the problem of the toxicity of such products. If a fire is relatively small and soon extinguished, many such species may remain in the surroundings in significant quantities, thus posing a health risk which can be as important as the original fire. The most serious risk is that of halogenated derivatives. Their mode of action involves their decomposition into halide radicals, which eventually combine to form species such as HX or X_2 (where X is a halogen) when the fire is extinguished[25]. This, of course, can also happen when the flame retardant materials come to be destroyed by incineration. Other important pollutants produced by the pyrolysis of halogenated aromatic compounds are the polyhalogenated dibenzofurans and dioxins[26]. Studies have shown that these species are produced from common flame retardant materials, e.g. tetrabromobisphenol-A or decabromodiphenylether, in quite large quantities (up to 10% yield, but usually lower) by low temperature (around 400-500°C) pyrolysis. The presence of synergists, such as Sb_2O_3, seems to enhance their formation, and the presence of gaseous oxygen has little effect[27,28]. The presence of a halogen ortho to an oxygen atom on the aromatic ring seems to favour the formation of furans and dioxins, although the mechanism of formation is not fully understood. It can be seen that small, low temperature fires, or inefficient incineration[29] could lead to significant amounts of these species, and this is currently giving rise to a great deal of concern over the use of polyhalogenated aromatic compounds in flame retardant applications.

The last consideration is that of afterglow, which is particularly important for textiles. The oxidation of a fabric takes place in two stages:

1) the burning of the volatile degradation products to form gases and a solid, carbonaceous char

2) the high temperature oxidation of this char, which occurs after the flame has been extinguished, and could eventually consume the whole material if left unchecked.

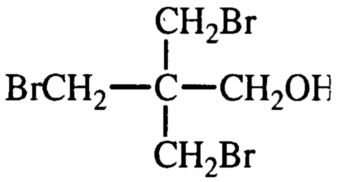
This phenomenon is familiar to all in the form of a candle, in which the wick may continue to glow for some considerable time after the candle has been extinguished, often giving off acrid smoke. To be effective, then, a flame retardant must also prevent afterglow.

1.8 The Present Study

From the introduction above, it can be seen that flame retardants are of vital importance in the modern world, and are becoming increasingly so, but that they also present serious problems, particularly regarding safe methods of disposal. The most widespread and generally useful types of flame retardants are those consisting of a halogenated organic material in combination with an inorganic synergist such as antimony or phosphorus. Bromine is the most effective halogen, being approximately twice as effective as chlorine[11]. There are conflicting views on whether aliphatic or aromatic compounds are more effective as flame retardants, or whether it is in fact important at all. The use of aromatics provides a higher thermal stability, but raises the problem of toxin production on decomposition, whereas aliphatics greatly reduce this problem[30,31]. The synergist is usually included as a separate additive, i.e. in a separate molecule from the halogen.

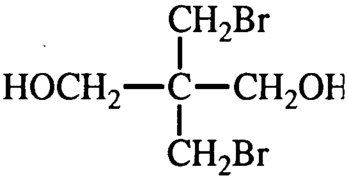
It was thus thought to be of interest to synthesise and characterise a series of brominated main group alkoxides for screening as potential flame retardants. In this way, the bromine would be present in the same molecule as the potential synergist, which may increase the efficiency of the retardant mechanism. The alcohols chosen to be used were:

a) **3-bromo-2,2-bis(bromomethyl)propan-1-ol**
(tribromoneopentyl alcohol, TBNA, $(CH_2Br)_3C.CH_2OH$)



$$\begin{array}{ccccc} & & CH_2Br & & \\ & & | & & \\ BrCH_2 & - & C & - & CH_2OH \\ & & | & & \\ & & CH_2Br & & \end{array}$$

b) **2,2-bis(bromomethyl)-1,3-propanediol**
(Dibromoneopentyldiol, DBND, $(CH_2Br)_2C(CH_2OH)_2$)



$$\begin{array}{ccccc} & & CH_2Br & & \\ & & | & & \\ HOCH_2 & - & C & - & CH_2OH \\ & & | & & \\ & & CH_2Br & & \end{array}$$

Such derivatives would have several advantages

1) Synergist in close proximity to the halogen
2) TBN-O- groups sterically bulky, leading to hydrolytic stability
3) Aliphatic bromine, so no dibenzofurans or dioxins

4) High bromine content (60-70% w/w)
5) Ease of formulation, being only one compound.

Disadvantages may be:

1) Loss of control over precise bromine:synergist ratio

2) Aliphatic, so a lower decomposition temperature than aromatics.

The elements and systems studied were chosen for their current use in flame retardant compounds and were, in approximate order of importance: phosphorus, boron, aluminium, silicon, zinc, titanium, (magnesium). Some borazine derivatives were synthesised, and the 4-bromophenoxy analogues of some of the silicon species were also prepared in order to compare the two systems.

The derivatives prepared were mainly discrete molecular compounds, many of which were liquids at room temperature, and thus of limited utility as flame retardant additives in themselves. However, it may be possible to link these discrete units to form oligomers or even polymeric materials. In this way, the basic structural unit could be retained, while the melting point of the resultant material could be tailored to be suitable for a particular system by controlling the chain length of the polymer. This would be of particular interest for the silicon species, as they could possibly form stable, functionalised silicone polymers.

1.9 References

1) "Jericho", JR Bartlett, Lutterworth Press, 1982, p.93.
2) "ΑΙΝΕΙΟΥ ΠΟΛΙΟΡΚΗΤΙΚΑ", LW Hunter, OU Press, 1927, pp.90-3.
3) "Aineias the Tactician", D Whitehead, Clarendon Press, Oxford, 1990, pp.8-9.
4) O Wyld, Brit. Pat. 551 (1735).
5) JL Gay-Lussac; Ann. Chem. Phys., 1821, 18(2), 211.
6) WH Perkin; J. Ind. Eng. Chem., 1913, 5, 57 & WH Perkin; Met. Chem. Eng., 1912, 10, 636.
7) e.g. RF Simmons & E Metcalfe; Chem. in Brit., 1987, 3, 230-4.
8) "Polymer Processing"; DH Morton-Jones; Chapman & Hall, London, 1989, Chapter 3, pp.55-73.
9) Kirk-Othmer Encyclopedia of Science and Technology, 3rd Ed., 10, 349.
10) e.g. ER Larsen; Fire Retard. Chem., 1975, 2(4), 209-23.
11) GL Nelson & JL Webb; J. Fire. Flammability, 1973, 4(Oct.), 325-43.
12) e.g. CA 54:P21852g, 55:P17082i
13) SL Madorsky, "Thermal Degradation of Organic Polymers", Wiley-Interscience, New York, 1963. M Lewin & A Basch in M Lewin, SM Atlas & EM Pearce eds., "Flame Retardant Polymeric Materials", Vol. 2, Plenum Press, New York, 1978, pp.1-3.
14) AW Benbow & CF Cullis; Combust. Flame, 1975, 24, 217.
15) ER Larsen; J. Fire. Flammability/Fire Retard. Chem., 1974, 1, 4
16) JW Lyons, "The Chemistry and Uses of Fire Retardants", Wiley-Interscience, New York, 1970, pp.14-17. EC Creitz, J. Res. Natl. Bur. Stand., 1970, 74A, 521. G Avondo, C Vorelle & R Delbourgo; Combust. Flame, 1978, 31, 7.
17) I Touval; Am. Chem. Soc., Prepr. Org. Coat. Div., 1971.
18) J Pitts, PH Scott & J Powell; Cell. Plast., 1970, 6, 35.
19) CP Fenimore & FJ Martin; Combust. Flame., 1966, 10, 135.
20) I Einhorn; "The flammablity of polymeric materials", Lecture series, University of Utah, 1970.
21) JP Reid, WA Reeves & JG Frick; US Dept. Agric. Leaflet no. 454, USDA, Washington DC, 1959.
22) JRW Perfect; J. Soc. Dyers & Colour, 1958, 74, 829.

23) EC Clayton & LL Heffner (Wm. E Hooper & Sons, Co.), US 2,229, 612.

24) Kirk-Othmer Encyclopedia of Science and Technology, 3rd Ed., 10, 401-2.

25) ER Larsen & RB Ludwig; J. Fire Flammability, 1979, 10, 69.

26) D Pitea, L Bonati, U cosentino, M Lasagni & G Moro; Toxicol. Environ. Chem., 1989, 22(1-4), 239-61.

27) D Bieniek, M Bahadir & F Korte; Heterocycles, 1989, 28(2), 719-22.

28) R Dumler, H Thoma, D Lenoir & O Hutzinger; Chemosphere, 1989, 19(12), 2023-31.

29) e.g. Kirk-Othmer Encyclopedia of Science and Technology, 3rd Ed., 13, 182-206.

30) M Ravey, T Fischler & M Kramer; Fire Mater., 1978, 2(1), 34-6.

31) T Kaino; Rev. Electr. Commun. Lab., 1977, 25(1-2), 71-8.

CHAPTER TWO

2 The Synthesis of Derivatives of 3-Bromo-2,2-bis(bromomethyl)-1-propanol - Boron and Borazine Derivatives

2.1 General Introduction

Alkoxides are defined as the class of compounds containing at least one M-O-C group, where M is a metal or metalloid. The first members of this group were prepared in the mid nineteenth century, when Ebelman and Bouquet prepared alkoxides of boron and silicon by direct reaction of the covalent chlorides with alcohols[1,2]. Boron oxide was used in place of the chloride in 1867 in the synthesis of triethoxy boron[3], and direct synthesis from the metal with an alcohol was achieved in 1869 when Lamy prepared triethoxy thallium[4]. These methods were found to be generally applicable to many metals and metalloids, along with the reaction of the M(OH) group with alcohols with elimination of water, and the related alcohol interchange reaction of an alkoxide with another alcohol. The main synthetic routes to alkoxides can thus be summarised as below:

1) Metal + alcohol

$$M + n\,ROH \longrightarrow M(OR)_n + {}^{n}/_{2}\,H_2$$

2) Covalent metal halide + alcohol

$$MX_n + n\,ROH \longrightarrow M(OR)_n + n\,HX$$

3) Metal oxide/hydroxide + alcohol

$$MO_n + 2n\,ROH \longrightarrow M(OR)_{2n} + n\,H_2O$$

$$M(OH)_n + n\,ROH \longrightarrow M(OR)_n + n\,H_2O$$

4) Metal alkoxide + alcohol

$$M(OR)_n + n\,R'OH \longrightarrow M(OR')_n + n\,ROH$$

Not all of these methods will work for all metals and all alcohols, and there are also several more specialised routes to particular alkoxides, e.g. the controlled oxidation of trialkylaluminium compounds to their trialkoxy aluminium analogues. However, the routes outlined above are the most widely applicable.

Method 1 works well only for metals of low electronegativity, such as the alkali metals or alkaline earths. As the electronegativity of the metal increases, a catalyst may be required, as in the case of aluminium. If this does not work, method 2, using a covalent halide, may be successful, though a base may be required to remove the hydrogen halide formed and thus aid the reaction. Method 3 may be forced by continuous removal of water, e.g. as an azeotrope, and can be used with metals of relatively high electronegativity. The last method is useful for the synthesis of higher alkoxides from lower ones, which may be easier to make, and may also be forced by continuous removal of the more volatile alcohol formed in the reaction.

As well as the electronegativity of the metal, the choice of synthetic route will also be affected by the alcohol concerned; principally as a result of the inductive effect of the organic group and its steric requirements. For example, reaction rates of metal halides with alcohols tend to go in the order:

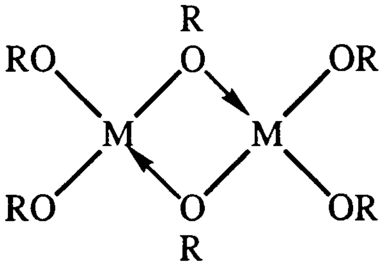
primary > secondary > tertiary

This can be explained by the alcohols becoming less acidic due to the increased +I effect of the organic group. Also, the more sterically demanding the organic group, the more forcing the conditions will need to be to force the reaction towards completion. For example, the simple reaction of silicon tetrachloride with t-butanol tends to give impure mixtures of the lower butoxides, with t-butyl chloride resulting from a side reaction of t-butanol with the hydrogen chloride produced. The use of pyridine to remove the hydrogen chloride immediately on formation allows the reaction to proceed to the pure tributoxide, but the bulk of the t-butoxy group prevents the formation of the tetrabutoxide, although the final chlorine can be replaced by a smaller alcohol, such as ethanol[5]. Similarly, titanium tetrachloride fails to give pure t-butoxides, even in the presence of ammonia to remove the hydrogen chloride, and both pyridine and ammonia are necessary to force the reaction[6].

The physical properties of metal alkoxides are also governed to a large extent by the identities of the metal and the organic group. The M-O bond is highly polar, and would be expected to show a high degree of ionic character, particularly for highly electropositive elements like the alkali metals. However, these alkoxides usually display properties more characteristic of covalent compounds; for example, they are often soluble in common organic solvents, and show reasonably high volatilities. These observations suggest that the polarity of the M-O bond is somehow being reduced, and this can be explained in two ways:

1) The inductive effect of the organic group tending to release electrons to the M-O bond, decreasing its polarity.

2) The formation of intermolecular dative M-O bonds, reducing the electron density on the oxygen and thereby reducing the polarity of the intramolecular M-O bond (see over)



These two factors are complementary to some degree, as the former would be expected to increase with branching within the organic group, whereas the latter would be expected to decrease, as the steric requirements make the formation of dative bonds more difficult.

The balance of these two effects has large implications for such properties as volatility, solubility, molecular complexity and crystal structure. For example, a metal t-butoxide would be expected to have less-polar M-O bonds due to the inductive effect of the t-butyl groups, and also to be less likely to form oligomers *via* dative bonding due to their steric bulk; it should thus be more volatile than the isomeric n-butoxide. Conversely, the n-butoxide may also form strongly bound oligomers, and may volatilise in this form, thus producing a volatility even lower than expected.

The structures of metal alkoxides are also dominated by the formation of oligomers *via* dative M-O bonds. Examples of oligomers up to octamer are known, along with examples of polymeric structures. The range of structures is huge, and which structural form an alkoxide takes is again dependent on the metal, the organic group, and so on. For example, potassium t-butoxide is tetrameric, having a cubane structure in which each potassium is bound to three t-butoxy groups[7]. Lithium methoxide has a planar polymeric structure where each lithium is bound to four oxygen atoms and *vice versa*, with the methyl group lying above the oxygen[8]. Interestingly, as each MeO$^-$ group is bound to four lithium atoms, yet has only three electron pairs, the bonding is characteristic of that in other electron deficient materials, such as carboranes. Aluminium tri(t-butoxide) is dimeric, forming a structure similar to that of the familiar Al_2Cl_6[9], the steric bulk of the t-butyl groups preventing the formation of higher oligomers, such as those seen in the trimeric and tetrameric forms of aluminium tri(isopropoxide)[10]. Interestingly, $Al(OCH_2CH_2Cl)_3$ also forms a dimer, although on pure steric grounds it might be expected to have a similar molecular complexity to the tetrameric $Al(OCH_2CH_3)_3$. This difference has been explained by the electron withdrawing effect of the electronegative chlorine, reducing the ability of the oxygen atoms in the M-O bond to form intermolecular dative bonds.

Structural data for metal alkoxides are often gained *via* indirect methods such as NMR, IR and mass spectroscopy, rather than direct methods such as single crystal X-ray crystallography. These techniques can give a valuable insight into the nature of the material under study, and how its structure can vary from the solid to the liquid state or even over time.

NMR spectroscopy is used mainly to study the protons in the organic group of alkoxides, but NMR active metal nuclei can also yield valuable structural information. ^1H NMR is particularly useful when both terminal and bridging alkoxy groups are present, as the different signals from the corresponding protons in the two environments can often be identified and can provide support for or rule out a particular structure for the molecule. If this effect cannot be observed under normal conditions, it can often be resolved at low temperatures, when fluxional and exchange processes are slowed down. Similarly, metal NMR, e.g. ^{7}Li, ^{11}B, ^{27}Al, etc., can be used to identify metals in differing environments, e.g. tetrahedral and octahedral coordination.

IR spectroscopy is useful principally in the absorption regions of the C—O and M-O bonds, the C-O bands generally being the more useful simply because they are easier to assign. The ν_{co} band in alkoxides generally falls in the range 900-1150 cm^{-1}, but its exact position for a particular species is determined by the alkoxy group. The exact frequency of the ν_{co} and ν_{mo} bands will also depend on the particular environment of the bond. For example, the bands for an MOC group involved in bridging dative bonds *via* the oxygen atom would be expected to be different from those of a terminal group, the bridging frequencies being lower than the terminal due to the lowering of the electron density in the bond and thus its strength and vibrational frequency.

Mass spectroscopy is most often used in order to determine the molecular complexity of a particular alkoxide, as the molecular ion observed usually corresponds to the structure of the alkoxide itself. However, an oligomer may also break up into monomers and smaller fragments before being detected. The fragmentation pattern observed can sometimes provide structural information, e.g. on which groups in a mixed, oligomeric alkoxide are in the bridging positions.

The chemical reactions of metal alkoxides are predominantly those with species containing reactive protons, usually in the form of the hydroxyl group. The nett reaction is substitution of the alkoxy group:

$$M(OR)_n + n\,HY \longrightarrow M(Y)_n + n\,ROH$$

The most common reaction of this type is hydrolysis, most alkoxides being extremely sensitive to water due to the polar M-O bond, which leaves the metal very susceptible to nucleophilic attack. A variety of other reagents can also attack alkoxides, such as diols, acids, amines, thiols, etc., but the presence of atmospheric moisture means that great care must be taken in handling the alkoxides to avoid hydrolysis.

Metal alkoxides have also found many uses as diverse as industrial catalysts and paint modifiers. Well known uses in preparative organic synthesis include the Meerwein-Ponndorf-Verley and Tischenko reactions, which both use metal alkoxide catalysts. Their use as flame retardants, utilising brominated alkoxy groups, is relatively new, but the following chapters will describe work undertaken in this area using many of the techniques outlined above.

2.2 Background

This chapter details the efforts that were made to synthesise derivatives of the brominated alcohol, 3-bromo-2,2-bis(bromomethyl)-1-propanol (tribromoneopentyl alcohol, TBNA). The alcohol was supplied by the Associated Octel Co. of Ellesmere Port with a view to synthesising stable, solid derivatives as potential flame retardants, as mentioned in the introduction. Most of the derivatives were those of main group elements, although those of certain other elements were studied, e.g. titanium, mainly due to previously recorded use in flame retardant applications. Many of the derivatives produced, especially those of silicon, were liquids, and thus of limited use in flame retardant applications, though some of these species were interesting for the trends they showed across a series, e.g. the methyl silane derivatives. Some of the materials produced, e.g. the mixed phenoxy/4-bromophenoxy silane derivatives, were expected to be mixtures, or compounds of an indefinite stoichiometry, so extensive purification was sometimes not undertaken, and this is occasionally reflected in the results of analyses. The aim, as stated above, was to produce stable, solid derivatives for further tests, and mixtures of compounds, if they could be produced reproducibly, were valid for this use. Some compounds were rigorously purified, e.g. the borazine derivatives, which were of interest as novel compounds.

Early work on TBNA was concerned with its use as a drug (cf. DBND) to control blood pressure. However, work progressed on the utilisation of TBNA in flame retardant systems mainly for polyurethanes[11] and polyesters[12]. The combination of the 3-bromo-2,2-bis(bromomethyl)-1-propoxy (TBNO) group into compounds of main group elements mainly involved phosphorus, although there is a patent covering the production of $B(OTBN)_3$ and its use as a flame retardant in polypropylene[13]. Various phosphorus derivatives have been studied, including the phosphate[14] and phosphite[15]. Dialkyl siloxanes with chain-terminating TBNO groups have also been studied[16].

2.3 General Experimental

Synthetic work was carried out under an atmosphere of dry nitrogen unless otherwise stated, in either a glove box or by use of a vacuum or nitrogen line. Materials were treated as hydrolytically unstable until shown to be otherwise, and were stored under dry nitrogen. IR spectra were taken on Perkin Elmer 377 or 577 grating IR spectrometers. NMR spectra were taken on a multi-nuclear Bruker AC250 NMR spectrometer. DSC analysis was performed using a Mettler FP 85 thermal analysis cell with a FP 80 central processor.

2.4 Preparation of Boron Derivatives

2.4.1 Preparation of Tris(3-bromo-2,2-bis(bromomethyl)-1-propyl)orthoborate, $B(OTBN)_3$

2.4.1.a Method 1

In a typical reaction, 42.23g (130mmol) TBNA was weighed into a clean, dry flask under nitrogen and dissolved in 100ml dry dichloromethane. To the stirred solution was added dropwise at room temperature a solution of 40mmol boron trichloride in dichloromethane (40.0ml @ 1M). On mixing, there was a reaction which evolved a colourless gas, but no significant exotherm. On completion of addition, the solution was stirred overnight to yield a white precipitate. Filtration gave a white solid, which was dried *in vacuo*. Concentration of the solution yielded further crops of solid.

$\underline{B(OTBN)_3}$:

Typical mass = 21.49g (first crop). Expect $B(OTBN)_3$ = 40mmol (39.29g)
so 55% yield on first crop.

Melting point.: **130-2°C**

MS: **EI - 214, 133, 53 (100%)**
CI+ - 124, 108 (100%), 94, 85, 78, 77, 58, 52, 44.

^1H NMR, δ (integration): **3.54 s (1), 3.93 s (3).**

^{13}C NMR, δ: **34.2, 43.6, 63.1.**

^{11}B NMR, δ: **18.2 (broad, FWHH ~ 400Hz).**

IR (cm^{-1}): **3000 vw, 2960 w, 2900 w (νCH aliphatic), 1470 m, 1410 s (δCH), 1340 vs ($\nu_{asym}BO$), 1300 s, 1270 m, 1250 m, 1245 m, 1220 m, 1190 m, 1150 w, 1075 m, 1050 s (νCO), 1015 m, 935 w, 855 s, 840 s, 815 w, 805 w, 705 w, 665 m, 630 s, 605 s, 585 w, 490 m, 480m** (see page A-1).
Unchanged on exposure to air for thirty minutes.

Analysis (%): B 1.01, C 18.29, H 2.46, Br 52.44^D, 59.66^D, 50.26^D, 71.8^O. (^{D} = analyses performed in Durham, ^{O} = analyses performed by Octel).
Calculated for $B(OTBN)_3$: B 1.10, C 18.34, H 2.46, Br 73.21.

2.4.1.b Method 2

In a typical preparation,19.19g (59mmol) TBNA was ground together with1.21g (20mmol) boric acid to form an intimate mixture. This was then placed in a dry flask and dried in vacuo at 50°C for one hour to remove the adsorbed moisture. After purging the reactants three times with dry nitrogen, 100ml dry toluene was added, which dissolved the

TBNA on stirring but left the boric acid in suspension. A distillation apparatus was then fitted to the flask and purged with dry nitrogen. The stirred suspension was then heated in an oil bath. The solution began to boil at a bath temperature of 110°C, and the first fraction of distillate came over at a bath temperature of ~125°C, at a still-head temperature of 84°C (lit. 84.1°C for water/toluene azeotrope). Some boric acid still remained undissolved/unreacted when the second fraction began to distil over at 110°C (toluene), so heating was continued until ~50ml distillate had been collected. By this time, all the boric acid had reacted, and cooling yielded a clear, colourless solution. The distillation apparatus was washed down with distillate to remove any remaining water. Removal of solvent from the solution under reduced pressure yielded a white solid, which was dried *in vacuo*. The volume of water recovered was generally around 90-95% of that expected for $B(OTBN)_3$ production, the remainder remaining on the walls of the condenser.

<u>$B(OTBN)_3$</u>:

Typical mass = 19.38g. Expect $B(OTBN)_3$ = 19.35g, so 100% yield.

M. Pt.: 130-2°C.

MS: The mass spectrum is identical to that of the product prepared by method 1.

^1H NMR: Again, as in section 2.4.1.a, but occasionally showing a weak signal at δ: 3.72 corresponding to the CH_2O protons of the free alcohol, though a signal due to free OH was never observed.

^{11}B NMR: As in section 2.4.1.a, with some variation of peak width.
^{13}C NMR: As in section 2.4.1.a.

Typical analysis (%): B 1.11, C 18.81, H 2.53, Br 64.88.
(Calculated for $B(OTBN)_3$: B 1.10, C 18.34, H 2.46, Br 73.21).

2.4.2 Preparation of Tris(3-bromo-2,2-bis(bromomethyl)-1-propyl)metaborate, $(TBNOBO)_3$, and Attempted Preparation of Polyborates

General Method

In a typical reaction, the required amounts of boric acid and TBNA were ground into a fine, intimate powder mixture in a pestle and mortar. The mixed reactants were then placed in a flask and heated to 50°C in vacuo for one hour to remove any adsorbed moisture, and the flask was then purged three times with dry nitrogen. 100ml dry toluene was added and the suspension stirred for 15 minutes, dissolving the TBNA and dispersing the boric acid into a fine suspension. This was necessary due to the tendency of boric acid to aggregate into clumps on the addition of toluene, which would then present a smaller surface area for reaction, reducing the efficiency of the process and lowering the effective boric acid:TBNA ratio. A still head and condenser were then fitted to the flask and purged with dry nitrogen for 15 minutes before the stirred suspension was heated using an oil bath. Generally, bath temperatures of ~130-40°C were needed for the vigorous reflux required to produce a reasonable rate of distillation. Aluminium foil cladding was also useful to minimise heat losses. The temperature at which the first fraction distilled was 84°C, and the second 110°C, corresponding to water/toluene azeotrope and toluene, respectively. Heating was generally continued until approximately half of the solvent had distilled across. During the distillation, the solution tended to become clearer as the boric acid reacted/dissolved. On cooling the solution, a precipitate often appeared, which could be filtered off and dried in vacuo while the solvent was removed from the solution under reduced pressure, yielding a further crop of solid. The distillation apparatus was washed repeatedly with distillate to remove the water from the walls of the condenser. The volume of water collected could then be measured.

2.4.2.a Reaction with 1:1 Ratio of $B(OH)_3$:TBNA

2.4.2.a(i) Reaction without intimate grinding of reactants.

The general reaction method was used, but without grinding the reactants. In this case, the aggregation of the boric acid was a major factor in the reaction. Several lumps of boric acid remained even after distillation had been continued to remove half the volume of solvent. At this point, heating was discontinued as the acid was not likely to dissolve in a decreasing amount of solvent. The volume of water isolated tended to be midway between that expected for orthoborate formation and metaborate formation. On cooling the reaction solution, a white solid crystallised and could be isolated and dried *in vacuo*. Removal of solvent from the remaining solution under reduced pressure yielded a further crop of white solid.

White crystalline solid - first crop:

M. Pt.: Softens 84°C, melts 102-108°C (clear liquid 150°C, indicating possible suspension of higher melting material in the molten sample).

IR (cm^{-1}): 1605 w*, 1470 s, 1430 s,1410 s (δ CH), 1375 m, 1360 s, 1345 vs (ν BO), 1305 s, 1290 m, 1270 m, 1250 m, 1245 m, 1225 m, 1190 m, 1150 w, 1075 m, 1055 m (ν CO), 1020 m, 940 w, 855 m, 845 s, 820 w, 810 w, 725 s*, 690 w, 670 w, 635 m, 605 m, 575 w, 485 m, 470 w, 455 w.
N.B. bands marked * are due to residual toluene.
After exposure to air, an νOH band appeared at ~3200cm^{-1}, but the remainder of the spectrum was unchanged.

^{1}H NMR, δ (integration): 3.52 s (109), 3.92 s (27), 4.05 s (7).

^{11}B NMR, δ: 17.8.

^{13}C NMR, δ: 34.3, 43.7, 63.1.

Analysis (crude, %): B 0.45, C 22.85, H 2.94, Br 61.52.
Calculated for B(OTBN)$_3$: B 1.10, C 18.34, H 2.46, Br 73.21.
Calculated for (TBNOBO)$_3$: B 3.08, C 17.13, H 2.30, Br 68.36.

<u>White solid - second crop:</u>

M. Pt.: 116-20°C

IR (cm^{-1}): 3220 s (ν OH), 1465 s (δ CH), 1380 s, 1350 vs (ν BO), 1310 s, 1290 m, 1280 m, 1255 m, 1250 m, 1230 m, 1190 s, 1150 w, 1080 m, 1060 s (ν CO), 1020 m, 940 w, 885 w, 860 s, 850 s, 810 s, 690 m, 670 m, 640 m, 610 s, 590 w, 550 w, 500 m, 480 w, 470 w.
There is also a very broad absorption around 800cm^{-1} which obscures some detail. This may be due to boric acid. Prolonged exposure to air yields bands due to TBNA.

^{1}H NMR, δ (integration): 3.53 s (75), 3.74 s (5), 3.92 s (20).

Analysis (crude, %): C 16.04, H 3.25.
Calculated for B(OTBN)$_3$: B 1.10, C 18.34, H 2.46, Br 73.21.
Calculated for (TBNOBO)$_3$: B 3.08, C 17.13, H 2.30, Br 68.36.

2.4.2.a(ii) Reaction with ground reactants.

The general method as outlined above was used in this case, with recovery of the white solid precipitated on cooling the reaction solution and that obtained on removal of the remaining solvent *in vacuo.*

White solid - first crop:

M. Pt.: Softens 110C, melts 120-30°C.

IR (cm^{-1}): 1470 s, 1445 s, 1415 s (δ CH), 1380 s, 1365 s, 1350 vs (ν BO), 1310 s, 1280 m, 1255 m, 1250 m, 1230 m, 1190 m, 1155 w, 1095 w, 1080 m, 1060 m (ν CO), 1020 w, 940 w, 860 s, 850 s, 820 w, 815 w, 730 s, 720 w, 695 w, 670 w, 640 m, 610 m, 500 w, 480 w, 470 w.

Exposure to air causes the appearance of a band at 3220cm^{-1} (ν OH), and the disappearance of the band at 730cm^{-1} (due to toluene).

^{1}H NMR, δ (integration): 3.54 s (108), 3.93 s (22), 4.06 s (8).

^{13}C NMR, δ: 34.0, 34.2, 43.7, 63.1, 63.7.

^{11}B NMR, δ: 18.6 (FWHH = 480Hz).

Analysis (%):	B 1.97, C 17.42, H 2.37, Br 64.73.
Calculated for $B(OTBN)_3$:	B 1.10, C 18.34, H 2.46, Br 73.21.
Calculated for $(TBNOBO)_3$:	B 3.08, C 17.13, H 2.30, Br 68.36.

White solid - second crop:

M. Pt.: Softens 88°C, melts 110-30°C.

IR (cm^{-1}): 1510 m, 1480 s, 1460 s, 1445 s, 1465 s (δ CH), 1350 s (ν BO), 1310 m, 1250 m, 1225 m, 1190 w, 1090 s (ν CO), 1070 m, 1060 w, 1020 w, 935 w, 900 w, 860 m, 850 m, 840 m, 815 m, 790 w, 735 m, 730 s, 720 s, 710 s, 680 w, 660 w, 645 w, 610 m, 485 w, 450 w, 395 w.

Unchanged on exposure to air apart from the appearance of a weak band at ~3400cm^{-1} (ν OH).

^{1}H NMR, δ (integration): 3.54 s (193), 3.93 s (7), 4.06 s (58).

^{13}C NMR, δ: 34.0, 34.2, 43.7, 63.2, 63.8.

^{11}B NMR, δ: 19.9 (FWHH = 670Hz).

Analysis (%):	B 3.65, C 15.85, H 2.65, Br 64.49.
Calculated for $B(OTBN)_3$:	B 1.10, C 18.34, H 2.46, Br 73.21.
Calculated for $(TBNOBO)_3$:	B 3.08, C 17.13, H 2.30, Br 68.36.

2.4.2.a(iii) Reaction using ground reactants and removal of all the solvent.

The general method as outlined above was used again, but instead of only continuing the distillation until approximately half of the solvent had distilled across, heating was continued until no more toluene could be recovered. The reaction vessel was then placed under vacuum to remove the remaining solvent and leave a white solid. This was suspended in 100ml toluene and warmed to ~50°C before being filtered to remove the undissolved solid. Removal of the solvent from the remaining solution *in vacuo* yielded another crop of white solid.

White solid - first crop:

M. Pt.: 140-5°C.

IR (cm^{-1}): 1505 w, 1460 s, 1445 s, 1410 s (δ CH), 1350 vs (ν BO), 1310 s, 1275 m, 1250 m, 1225 m, 1185 m, 1150 w, 1090 m (ν CO), 1070 w, 1060 w, 1020 w, 930 w, 900 w, 860 m, 850 m, 840 m, 815 w, 790 w, 730 m (B_3O_6 out-of-plane ring bend band), 720 m (B_3O_6 out-of-plane ring bend band), 660 w, 640 w, 605 m, 575 vw, 470 w, 440 vw (see page A-2).

^{1}H NMR, δ (integration): 3.55 s (42), 3.93 s (3), 4.07 s (11).

^{13}C NMR, δ: 34.0, 34.2, 43.7, 43.8, 63.1, 63.7.

^{11}B NMR, δ: 18.6.

Analysis (%): B 2.89, C 16.95, H 2.22, Br 63.72.
Calculated for $B(OTBN)_3$: B 1.10, C 18.34, H 2.46, Br 73.21.
Calculated for $(TBNOBO)_3$: B 3.08, C 17.13, H 2.30, Br 68.36.

White solid - second crop:
M. Pt.: 139-45°C

IR (cm^{-1}): 1505 m, [1465 s, 1445 s, 1415 s (δ CH)], ~1360 vs (ν BO), 1310 s, 1275 m, 1270 m, 1250 m, 1230 m, 1190 w, 1150 vw, 1090 s (ν CO), 1075 m, 1060 m, 1020 m, 930 w, 900 vw, 855 m, 850 s, 840 m, 815 m, 810 w, 790 w, 735 m, [730 s, 720 s (B_3O_6 out-of-plane ring bend band)], 710 m, 695 vw, 680 vw, 660 w, 640 w, 610 m, 585 w, 480 w, 450 w, 390 w.
After exposure to air (~30 minutes), a strong band appears at ~3200cm^{-1} (ν OH) and a band at ~830cm^{-1} obscures bands already there.

^{1}H NMR, δ (integration): 3.55 s (41), 3.93 s (2), 4.07 s (12).

^{13}C NMR, δ: 34.0, 43.7, 63.1, 63.7.

^{11}B NMR, δ: 18.6.

2.4.2.b Reaction with a 4:3 Ratio of $B(OH)_3$: TBNA

Attempt to produce a well defined polyborate

The general reaction method as outlined above was followed, distilling off approximately half the volume of solvent used, yielding the initial precipitate and the solid remaining in solution.

First crop of solid:
M. Pt.: 108-12°C.

IR (cm^{-1}): 3300 m (broad, ν OH), 1470 s, 1420 s (δ CH), 1350 s (ν BO), 1305 s, 1275 m, 1255 m, 1250 m, 1230 m, 1200 m, 1190 m, 1150 m, 1095 w, 1080 m, 1055 m (ν CO), 1020 m, 970 vw, 940 w, 860 m, 850 s, 820 m, 720 m (broad), 670 m, 635 m, 610 m, 585 w, 500 m, 480 m, 460 w, 420 w.
No change on exposure to air.

^{1}H NMR, δ (integration): [3.60 s, 3.62 s, 3.64 s (22.2 together)], 3.89 s (1.4), 3.97 s (1.0).

^{13}C NMR, δ: 35.2, 35.4, 35.5; 44.5, 45.0; 61.1, 61.3, 63.1, 63.3, 63.6.

^{11}B NMR, δ: 20.4

(All the NMR spectra in this case recorded using d_6 acetone as solvent).

Analysis (%):	B 6.83, C 16.02, H 2.39, Br 63.77.
Required for polyborate:	B 4.04, C 16.54, H 2.21, Br 66.18.

<u>Second crop of solid:</u>

M. Pt.: Melts 144-7°C.

IR (cm^{-1}): 1460 s (broad, δ CH), 1360 vs (broad, ν BO), 1245 s, 1225 s, 1185 m, 1150 m, 1090 s (ν CO), 1070 s, 1055 s, 1030 m, 1020 m, 930 m, 900 w, 855 s, 850 s, 840 s, 810 s, 790 m, [725 s, 710 s (B_3O_6 out-of-plane ring bend band)], 690 m, 660 m, 640 m, 605 s, 580 w, 490 w, 480 m, 465 w, 450 w, 390 w.
After exposure to air, a band appears at ~3200cm^{-1} (ν OH).

^{1}H NMR, δ (integration): [3.59 s, 3.62 s, 3.63 s, 3.64 s, 3.65 s (162)], [3.89 s, 3.95 s, 3.97 s, 4.01 s, 4.03 s, 4.05 s (33)].

^{13}C NMR, δ: 35.2, 35.4, 44.4, 44.9, 61.2, 63.2, 63.4, 63.7.

^{11}B NMR, δ: 20.3.

Analysis (%):	B 3.02, C 17.31, H 2.29, Br 65.94.
Required for polyborate:	B 4.04, C 16.54, H 2.21, Br 66.18.

2.4.2.c Reaction with 2:1 Ratio of $B(OH)_3$: TBNA

The general reaction method as detailed above was used with relatively small amounts of reactants (~15g) which were ground well to a powder before use. Also, heating was continued until distillation had ceased in order to give the maximum possible reaction time. The resultant white solid was dried *in vacuo*, stirred for an hour in 100ml hot toluene and filtered hot under suction to yield a white solid. Removal of the solvent from the filtrate under reduced pressure yielded a second crop of white solid.

Water isolated = 1.90ml

White solid - first crop:

Mass = 1.25g

M. Pt.: No change up to 150°C, then the sample appeared to decompose, giving a colourless vapour which condensed on the cool parts of the tube.

IR (cm^{-1}): ~3300 vs (broad, ν OH), ~1350 vs (broad, ν BO), 960 s, 940 s, 820 s, 720 s (B_3O_6 out-of-plane ring bend band), 650 s, 590 m, 470 m, 450 m, 410 m.

^1H NMR, δ: 3.56 s, 4.08 s. Both signals extemely weak.

^{13}C NMR: No signals

^{11}B NMR, δ: 20.5.

Analysis (%): B 22.55, C 2.25, H 2.22, Br 8.66.
Calculated for $(HOBO)_3$: B 24.67

White solid - second crop:

Mass = 12.30g.

M. Pt.: 139-44°C.

IR (cm^{-1}): 1505 w, 1480 s, 1440 s, 1410 s (δ CH), 1375 s, 1350 vs (ν BO), 1310 s, 1275 m, 1265 m, 1250 m, 1225 m, 1185 w, 1090 s (ν CO), 1070 m, 1060 w, 1020 w, 930 w, 900 vw, 855 m, 850 m, 840 m, 810 m, 730 m, 725 m (B_3O_6 out-of-plane ring bend band), 715 s (B_3O_6 out-of-plane ring bend band), 710 s, 660 w, 640 w, 610 m, 480 w, 450 w, 390w (see page A-3).
After exposure to air (cm^{-1}): 3200s (ν OH), ~1440 vs (broad, δ CH), 1350 s (ν BO), 1305 s, 1275 m, 1250 m, 1225 m, 1195 m, 1150 w, 1090 m (ν CO$_{\text{metaborate}}$), 1075 m, 1055 m (ν CO$_{\text{orthoborate}}$), 1020 m, 935 w, 880 w, 860 s, 845 s, 810 s (broad), 725 m, 715 m (B_3O_6 out-of-plane ring bend band), 660 w, 630 w, 610 m, 545 w, 495 w, 480 w.
On prolonged exposure, the spectrum reverts to that of $B(OTBN)_3$.

^{1}H NMR,δ (integration): 3.55 s (29), 4.07 s (8).

^{13}C NMR, δ: 34.0, 43.8, 63.7.

^{11}B NMR, δ: 18.9.

Analysis (%): B 3.09, C 17.79, H 2.29, Br 64.62.
Calculated for $B(OTBN)_3$: B 1.10, C 18.34, H 2.46, Br 73.21.
Calculated for $(TBNOBO)_3$: B 3.08, C 17.13, H 2.30, Br 68.36.

2.5 Preparation of Borazine Derivatives

2.5.1 Preparation of N-triphenyl-B-trichloroborazine, $(PhNBCl)_3$ by thermal elimination of HCl

37.48g (320mmol) boron trichloride was dissolved in 300ml dry toluene in a dry 500ml flask under nitrogen and the solution cooled to -30±5°C (dry ice/acetone bath). To this was added 30.0ml (330mmol) aniline, dropwise with stirring, to form a white precipitate. The suspension was allowed to warm to room temperature and refluxed for 20 hours. On heating, effervescence began at 70-80°C, evolving a colourless gas, and by 120°C, dissolution of the solid was virtually complete. On cooling to room temperature, crystallisation/precipitation began at ~80-70°C. Filtration of the cold suspension yielded a white solid and a pale yellow solution. The solid was dried *in vacuo* and purified by recrystallisation from boiling toluene.

White precipitate - $PhNH_2$:BCl_3 adduct:

Melting Point: Softens at ~140°C and appears to sublime, melts at 156°C. (Lit.: Begins to melt at 100°C, decomp. ~120°C[18] , decomp. 140°C[17] , decomp. 168-72°C[19].).

IR spectrum (nujol mull/KBr plates/prepared in nitrogen) cm^{-1}: 3220s, 3180s (νNH?) , 1605w, 1565s (δNH?)*, 1495m (δCH?), 1310s, 1290s, 1195m, 1190m, 1160w, 1080m, 1030w, 920m, 890s, 870s, 850m, 825s, 765m, 750s, 740s, 725m, 685s, 650s, 570s, 535s.
*N.B. TWO bands observed here, in contrast to Gerrard & Mooney, who specifically report only one[17].
Exposure to air leads to loss of detail through band broadening. Also bands appear at 2580cm^{-1} (NH^+?) & ~1450cm^{-1} (broad).

Analysis (crude product): B 4.83, C 36.37, H 3.71, N 6.78
(Calc. for $PhNH_2{:}BCl_3$, B 5.14, C 34.27, H 3.35, N 6.66).

White crystalline product - $(PhNBCl)_3$:

Melting point: Sinters at 267°C, melts at 278-82°C (lit. sinters 255-60°C, melts with decomp. 265-70°C[18.]).

IR spectrum (nujol mull/KBr plates/prepared under nitrogen) cm^{-1}: 1950w, 1875w, 1795w, 1735w (aromatic ring overtone/combination bands), 1600s (arom. ring bend?), 1495s, ~1400vs (broad, BN ring), 1265m, 1250m, 1175m, 1160s, 1120w, 1080m, 1030m, 1010w, 910w, 840s, 820m, 785w, 770w, 740w, 700vs, 680s, 615w, 560s (see page A-4).
After exposure to air for one hour, cm^{-1}: 3630m, 3600m (νNH?), 3200s (νOH?), 3040m (aromatic νCH), 2600s, 2570s (NH^+?), 2260w, 2020m, 1605m, 1600m, 1580w (arom. ring), 1490s, ~1425vs (borazine ring), 1220w, 1195m, 1175w, 1155w, 1110w, 1070w, 1060w, 1030m, 1005w, 960w.br., 920w, 880w, 790m, 740s, 720m, 695m, 680m, 645m, 615w, 570w, 560w, 545w, 525w, 510w, 490vw, 475m, 405m.

^1H NMR spectrum:
Many signals are seen between 7.04 & 7.34ppm.

^{11}B NMR spectrum: One signal at δ:31.2 (broad, FWHH ≈ 430Hz). Literature value, δ:31.5[20].

^{13}C NMR spectrum: δ: 125.8w, 127.6s, 128.3m, 129.5s, 130.3s, 143.8w.

Analysis (crude): C 53.09, H 3.85, N 10.17, Cl 24.26.
(pure sample): C 52.56, H 3.86, N 10.29, B 6.74, Cl 23.87.
(Calc. for $[PhNBCl]_3$, C 52.46, H 3.67, N 10.20, B 7.87, Cl 25.81).

2.5.2 Attempts to Prepare N-triphenyl-B-trichloroborazine, $(PhNBCl)_3$, using Base.

2.5.2.a Using diazobicyclooctane, DABCO, in dichloromethane.

20ml (@ 1.6M, 20mmol) boron trichloride in dichloromethane was syringed into a dry flask with 20ml dry dichloromethane under nitrogen. To this solution was added, dropwise with stirring at 0°C (ice bath), a solution of 2.24g (20mmol) DABCO and 1.8ml (20mmol) aniline in 40ml dichloromethane to give an exothermic reaction producing a white precipitate. The suspension was warmed to room temperature then refluxed for 2 hours before being allowed to cool. Filtration yielded a white solid and a pale yellow solution. The solid was dried *in vacuo* and the solvent removed from the solution under reduced pressure to give a pale yellow solid.

White solid:

Melting point: Chars at > 250°C.

IR spectrum (nujol mull/KBr plates/prepared under nitrogen),cm^{-1}: ~2350s (v. broad, NH^+), 1600w, 1495m, ~1400m (broad), 1230w, 1170w, 1055s, 990w, 980m, 955m, 930w, 895w, 850s, 820m, 800w, 755s, 740s, 690m.

Analysis (crude):	C 35.30, H 6.00, N 11.95, Cl 38.69.
(Calc. for DABCO.2HCl,	C 38.93, H 7.62, N 15.13, Cl 38.31).

Pale yellow product - $(PhNBCl)_3$:

Melting point: ~120°C

IR spectrum (nujol mull/KBr plates/prepared under nitrogen), cm^{-1}: 3380w (NH?), 1945w, 1870w, 1800w, 1735w (O/C bands), 1600s, 1590s (aromatic ring bends?), 1490vs, 1435vs, 1335s, 1315s, 1265s, 1220s, 1180s, 1160s, 1075m, 1030m, 1000w, ~970w, 900w, 840m, 820w, 760s, 750s, 735s, 700s, 680m, 625m, 560m.

Analysis (crude): B 4.97, C 57.60, H 5.03, N 11.08, Cl 16.43
(calc. for $[PhNBCl]_3$; B 7.87, C 52.46, H 3.67, N 10.20, Cl 25.81.
calc. for $[PhNBCl]_3{:}PhNH_2$; B 6.42, C 57.05, H 4.39, N 11.09, Cl 21.05).

2.5.2.b using triethylamine in toluene.

A solution of 1.8ml (20mmol) aniline and 5.6ml (40mmol) triethylamine in 20ml dry toluene was added, dropwise with stirring, to a solution of 20mmol (20ml @ 1.6M in hexanes) boron trichloride in 20ml toluene to yield a yellow precipitate and an orange solution. The solid was removed by filtration and dried in vacuo. Removal of the solvents from the orange solution under reduced pressure yielded an intractable brown solid.

Yellow precipitate:

Mass: 5.6g
Expect Et_3NHCl = 40mmol = 5.5g

Melting point: Chars at 200°C, appears to decompose ~245°C.

IR spectrum (nujol mull/KBr plates/prepared under nitrogen), cm^{-1}: 2600m, 2530w, 2490m (νNH^+), 1400m, 1175m, 1070w, 1040m, 850w, 810w, 700w.

Analysis (crude product): B 0.70, C 50.62, H 10.80, N 9.74, Cl 23.08
(calculated for Et_3NHCl; B 0.00, C 52.35, H 11.71, N 10.18, Cl 25.76).

Brown solid:

IR spectrum (nujol mull/KBr plates/prepared under nitrogen), cm^{-1}: 3400w (NH^+?), 1945w, 1870w, 1795w, 1740w (arom. O/C bands), 1600s (aromatic ring bend?), 1495s, 1155s, 1070s, 1025s, 835m, 800m, 750m, 730m, 695s, 615w, 560w. Very little detail. Bands at ~1000-1500cm^{-1} partially obscured by very broad absorption in that region.

2.5.3 Preparation of N-tris(4-bromophenyl)-B-trichloroborazine, $(pBrC_6H_4NBCl)_3$.

A solution of 39.58g (230mmol) 4-bromoaniline in 100ml dry toluene was added dropwise to a cold (-30±5°C, dry ice/acetone bath), stirred solution of 26.96g (230mmol) boron trichloride in 200ml toluene to produce a pale fawn solid in a fawn solution. The stirred suspension was refluxed overnight for 20 hours then allowed to cool. The hot solution yielded a pale fawn solid on cooling which was filtered off and dried *in vacuo* before being purified by recrystallisation from boiling toluene.

First crop of pale fawn solid - $4\text{-}BrC_6H_4NH_2{:}BCl_3$ adduct:

Melting point: first change at 158°C, material darkens from 166°C, melts 180-220°C. (cf. 4-bromoaniline, m.pt. 62-4°C)

IR spectrum (nujol mull/KBr plates/prepared under nitrogen), cm^{-1}: 3220m, 3150w (νNH?), 2680m, 2650m, 2560m, 2490w, 1590w, 1570m, 1550w, 1490s, 1365m, 1235w, 1200w, 1115w, 1070m, 1015m, 940w, 890w, 870m, 825w, 820w, 810m, 745w, 725m, 710w, 690m, 685m, 615w, 540m, 485m, 450w.
After exposure to air for one hour: 3210s, 2690m, 2560m, 1615w, 1590w, 1570w, 1490s, 1365m, 1310w, 1285w, 1235w, 1200m, 1120w, 1070m, 1015m, 940w, 870m, 810s, 800m, 750w, 725m, 695m, 685m, 620w, 545m, 490m, 450w.

Second crop of pale fawn solid - $(4\text{-}BrC_6H_4NBCl)_3$:

IR spectrum (nujol mull/KBr plates/prepared under nitrogen), cm^{-1}: 1905w, 1775w, 1660w (aromatic O/C bands), 1605w, 1590w (aromatic ring bend?), 1485s, 1380vs (broad), 1260s, 1170s, 1155s, 1115m, 1100m, 1070s, 1030w, 1010s, 940w, 830s, 725vs, 700s, 680s, 625w, 590s, 500s, 460m (see page A-5).
The spectrum is unchanged on exposure to air for 3 hours.

Analysis: Crude product:	B 3.89, C 37.26, H 2.36, N 5.23.
Recrystallised product:	B 3.89, C 39.43,H 2.58, N 5.52
(Calc. for $(pBrC_6H_4NBCl)_3$:	B 5.00, C 33.32, H 1.86, N 6.48).

Recrystallisation from hot toluene gives a 91% recovery of purified material.

2.5.4 Preparation of N-triphenyl-B-tris(3-bromo-2,2-bis(bromomethyl)-1-propoxy)borazine, $(PhNB\text{-}OTBN)_3$

In a typical preparation, a suspension of LiOTBN in toluene was prepared by the slow, dropwise addition of 12.6ml (@ 1.6M, 20.2mmol) butyl lithium in hexanes to a stirred solution of 6.53g (20.1mmol) TBNA in 20ml toluene. This reaction was performed at room temperature in order to keep the TBNA in solution in the toluene.

The temperature was controlled by the rate of addition of butyl lithium and a water bath. This yielded a slurry of LiOTBN in toluene/hexane which was mixed under dry nitrogen with 2.07g (5.0mol) $(PhNBCl)_3$ in 40ml toluene. The order of addition was not important, as there was no discernible reaction at room temperature. The stirred slurry was then heated to reflux for 48 hours before being cooled and filtered to yield a pale fawn solid and a yellow solution. Concentration and cooling of this solution yielded a yellow solid which was purified by recrystallisation from hot toluene. Alternatively, the solvents could be removed from the yellow solution and the crude yellow product recrystallised from hot toluene.

Pale fawn solid:

IR spectrum (nujol mull/KBr plates/prepared under nitrogen), cm^{-1}: 1410m (B-N?), 1325m, 1115w.
After exposure to air, very strong bands appeared at 3400 (νOH) & 1640 cm^{-1} (δOH), indicative of the absorption of water. This is seen with LiCl.

Yellow solid - $(PhNBOTBN)_3$:

Mass = 6.01g
Expect $(PhNB\text{-}OTBN)_3$ = 5.0mmol = 6.41g. So a 94% yield.
Recrystallisation from hot toluene gave a ~40% recovery rate.

Melting point: softens at ~130°C, melts at 161-4°C.

IR spectrum (nujol mull/KBr plates/prepared under nitrogen), cm^{-1}: 3080w, 3060w, 3020m (CH aromatic), 1945w, 1875w, 1805w (overtone/ combination aromatic ring bands), 1600s, 1590m (aromatic ring), 1490s, 1430vs, 1415vs, 1350vs, 1305s, 1275m, 1245m, 1225m, 1190m, 1170w, 1150w, 1115s, 1070m, 1055w,

1025m, 940w, 925m, 900w, 855s, 845s, 815s, 785m, 750s, 725s, 715s, 710s, 695s, 655m, 605s, 580s, 540m, 505m, 495w, 480m, 465m (see page A-6).
The spectrum remains unchanged on exposure to air for two hours.

^{1}H NMR spectrum:
Signals appeared at δ: 2.76s (CH_2Br), 2.88s (CH_2O) & ~7.26m (PhN).
The integral ratio of these three signals was 3.0:1.0:3.5 (calc. 3.0:1.0:2.5), and that of aliphatic:aromatic was 1.1:1.0 (calc. 1.6:1.0).
A signal also appeared at 2.34ppm, indicative of the methyl protons on toluene.

^{13}C NMR spectrum:
Signals appeared at δ: 33.8 (CH_2Br), 43.7 (C), 64.4 (CH_2O), 125.9 (para-C), 128.7, 129.3 (ortho & meta-C) & 143.4 (C-N).
Other signals also appeared at δ: 34.2, 34.5, 43.3, 63.2, 115.1 & 142.6 due to impurities. These were greatly reduced on longer reflux of the reaction mixture.

Analysis: Recrystallised product, C 33.57, H 3.52, N 3.11, Br 50.37, B 2.54.
(Calc. for $(PhBN\text{-}OTBN)_3$: C 31.03, H 3.08, N 3.14, Br 53.46, B 2.36,
and for $(PhBN\text{-}OTBN)_3.PhMe$: C 35.71, H 3.52, N 3.12, Br 53.45, B 2.41).

2.5.5 Preparation of N-tris(4-bromophenyl)-B-tris(3-bromo-2,2-bis(bromomethyl)-1-propoxy)borazine, $(p\text{-}BrC_6H_4NB\text{-}OTBN)_3$

In a typical preparation, 5.73g (17.6mmol) TBNA was dissolved in 80ml dry toluene and 11.0ml (@ 1.6M, 17.6mmol) butyl lithium in hexanes was added slowly with stirring at room temperature to produce a slurry of LiOTBN. To this was added under dry nitrogen purge 3.81g (5.9mmol) (p-$BrC_6H_4NBCl)_3$. The stirred suspension was then heated to reflux for 48 hours. Cooling and filtration yielded a white solid and a pale yellow solution. removal of solvents from the solution under reduced pressure gave an orange/yellow solid which was purified by recrystallisation from hot toluene.

White solid:

IR spectrum (nujol mull/KBr plates/prepared under nitrogen), cm^{-1}: 1485m, 1460m, 1325w, 1305w, 1290w, 1260w, 1240w, 1220w, 1110w, 1070w, 1010w, 845w, 790w.
After exposure to air for fifteen minutes, broad bands appeared at 3400 (νOH) & 1640 (δOH), indicative of the absorption of water by LiCl.

Orange/yellow solid - $(4\text{-}BrC_6H_4NBOTBN)_3$:

Mass = 6.52g
Expect (p-BrC_6H_4NB-OTBN$)_3$ = 5.9mmol = 8.93g. So a 73% yield.
Recrystallisation from hot toluene yielded ~40% recovery.

Melting point: 193-7°C

IR spectrum (nujol mull/KBr plates/prepared under nitrogen), cm^{-1}: 1900w (overtone/combination bands), 1590w (aromatic ring?), 1490s, 1475s, 1440s, 1415s, 1380vs, 1330s, 1310s, 1295s, 1275m, 1250m, 1230s, 1190w, 1170w, 1115s, 1105m, 1070s, 1015s, 940w, 920w, 865m, 850m, 840m, 830m, 820m, 795m, 785m, 725w, 720m, 715m, 710m, 660w, 615m, 605m, 520s, 480w (see page A-7).

After exposure to air for 2 days, and OH band appears at 3220cm^{-1}, accompanied by a general degradation of the spectrum and broadening of bands: 1620w, 1595w, 1485s, 1410s, 1350s, 1270m, 1250m, 1220m, 1190m, 1150w, 1110w, 1070m, 1055m, 1010m, 935w, 915w, 860m, 845m, 810m, 790m, 710w, 670w, 635m, 605m, 540w, 505w, 485m, 470w.

^{1}H NMR spectrum:
Signals appeared at δ: 2.82s (CH_2Br), 2.93s (CH_2O), 7.13d & 7.48d (aromatic ortho and meta protons).
The integration of CH_2Br:CH_2O:Aromatic was 3.0:1.0:2.5 (calc. 3.0:1.0:2.0). The ratio of aliphatic:aromatic was 1.9:1.0 (calc. 2.0:1.0).

^{13}C NMR spectrum:
Signals appeared at δ: 33.4 (CH_2Br), 43.7 (C), 64.7 (CH_2O), 119.6 (para-C), 130.8, 131.8 (ortho and meta-C), 142.2 (C-N).

Analysis: Recrystallised product:	C 27.89, H 2.81, N 2.65, B 1.94
[(p-BrC_6H_4NB-OTBN)$_3$:	C 26.18, H 2.40, N, 2.78, B 2.14.
(p-BrC_6H_4NB-OTBN)$_3$.PhMe:	C 29.91, H 2.76, N 2.62, B 2.02].

2.6 Discussion

2.6.1 Boron Derivatives

Tribromoneopentyl orthoborate (B(OTBN)$_3$, section 2.4.1) was a white, crystalline solid with a melting point above 100°C and thus showed early promise as a potential flame retardant. The IR spectrum on prolonged exposure to air showed that the species was also very hydrolytically stable, presumably due to the bulk of the TBNO groups around the boron atom, as otherwise, the electron-withdrawing effect of the nine bromine atoms might be expected to make the boron more reactive as a Lewis acid. The mass spectrum of the orthoborate shows signals at m/e 214 & 133, which are consistent with fragments containing Br_2 & Br respectively:

$(CH_2Br)_2C{=}CH_2$ m/e = 214, $(CH_2Br)(CH_2^+)C{=}CH_2$ m/e = 133

This suggests that the first step in the ionisation process is the detachment of the bulky TBNO groups from the boron atom, which then go on rapidly to decompose to give the Br_2 and Br-containing fragments, as no higher signals were seen. The pattern was, in fact, nearly identical to that of TBNA itself, but without the molecular ion peak at m/e 324. The fragmentation probably occurs via scission of the C-C bond adjacent to the O, yielding $(CH_2Br)_3C\cdot$, followed by loss of $Br\cdot$ to give the $(CH_2Br)_2C{=}CH_2$ unit, which gives the peak at m/e = 214. Further loss of $Br\cdot$ would yield the signal at m/e = 133/135, and loss of HBr would give the purely aliphatic signal at m/e = 53, corresponding to the fragment C_4H_5.

None of the signals in the CI^+ spectrum shows any isotope peaks, which would seem to rule out Br-containing fragments. There is the possibility that some of the signals are due to B-containing fragments, which survive due to the milder ionisation techniques. However, no molecular ion peak is visible, even so.

The 1:1 ratio of reactants used in section 2.4.2.a would be expected to produce the metaborate:

$$3\,\text{TBNA} + 3\,B(OH)_3 \longrightarrow (\text{TBNO-BO})_3 + 6\,H_2O$$

with the steric bulk of the TBNO- group perhaps even favouring the formation of the metaborate over the orthoborate. However, due to a number of factors, yields of the metaborate were not as high as were expected.

The volume of water isolated from these reactions was generally inconclusive, being midway between that expected for the ortho and metaborates. The water could result from reaction of the acid with the TBNA, or could be simply due to the decomposition of the orthoboric acid to give metaboric acid or boric oxide:

$$3\,B(OH)_3 \longrightarrow (HOBO)_3\ [+3\,H_2O] \longrightarrow B_2O_3\ [+1.5\,H_2O]$$

However, some form of ester interchange could also take place in the reaction of $B(OTBN)_3$ with boric acid to form $(TBNOBO)_3$ and H_2O:

$$3\,TBNA + B(OH)_3 \longrightarrow B(OTBN)_3 + 3\,H_2O$$

$$B(OTBN)_3 + 2\,B(OH)_3 \longrightarrow (TBNO\text{-}BO)_3 + 3\,H_2O$$

Complete reaction to yield solely metaborate and water, or solely orthoborate plus boric oxide plus water, would yield more water than no reaction of the TBNA at all, with just decomposition of the boric acid (for a 1:1 molar reaction, 2 mol vs. 1.5 mol). Thus, the amount of water isolated may be an indication of whether reaction of the TBNA has taken place or not, but is insufficient to identify the particular product formed.

From the data given above for the products of the 1:1 reaction with unground reactants (section 2.4.2.a(i)), it was evident that the major product of this reaction was the orthoborate. The amount of water produced, even allowing for a small amount to be left in the apparatus, precluded the formation of large yields of the metaborate and seemed to indicate a mixture of products. It also suggested that some of the boric acid had neither reacted nor decomposed.

IR evidence suggested that by far the major product was the orthoborate, the spectra being for the most part free of any other bands. The degradation of the second crop of solid on prolonged exposure to the atmosphere to give TBNA from what was seemingly the orthoborate indicates that it was more likely a mixture of products, mainly comprising the orthoborate but perhaps with some incompletely esterified boric acid. This would have a similar IR spectrum to the orthoborate and could have the effect of absorbing water from the air to hydrolyse the TBNO- groups to form TBNA, and perhaps even affect the orthoborate present to cause hydrolysis of the completely esterified species, this latter point being important as the orthoborate is indefinitely stable in air. This conclusion is supported by the ^{1}H NMR spectrum which indicated that the orthoborate was the only $CDCl_3$-soluble species present. For the first crop of solid, the ^{1}H NMR indicated that metaborate was present, which would hydrolyse in air to give the OH bands in the IR spectrum and provide for hydrolytic attack on the orthoborate, which was the major constituent. From the ratio of the two CH_2O signals, it would appear that up to 20% of this product was metaborate, though this was not evident from the IR spectrum, and does not take into account any $CDCl_3$-insoluble species present. Thus it appeared that the overall yield of metaborate from this reaction was $\leq$ 20%, the primary product being the orthoborate.

The isolation of unreacted boric acid/metaboric acid/boric oxide from the 1:1 reaction with finely ground reactants (section 2.4.2.a(ii)) indicated that quantitative reaction could not have taken place and that at least some orthoborate had been produced. The amount of water isolated was the maximum expected for either solely metaborate production or mixed products with dehydration of excess boric acid. This suggested that the solid isolated was probably mostly boric oxide, which would absorb moisture from the air to form the OH band observed in the IR.

The IR spectra of the first and second crops of product showed them to be mainly orthoborate and metaborate respectively. Both solids absorbed water on exposure to air, but not to the same extent as the first product from the reaction with unground reactants (section 2.4.2.a(i)), which suggested that they contained less unreacted or partially esterified acid. The ^{1}H & ^{13}C NMR spectra supported these conclusions, clearly showing that while both solids contained the same species, they were present in very different proportions in each. The ^{11}B NMR spectra also demonstrated the difference between the two species, with the metaborate resonating 1.3ppm downfield (to higher frequency) of the orthoborate. The fact that the first crop of product resonated at 18.6ppm rather than the 18.2ppm recorded for the pure orthoborate raised the possibility that some sort of exchange mechanism between the ortho and metaborates was taking place in solution:

$$3\,\mathrm{B(OTBN)_3} + 3\,\mathrm{H_2O} \longrightarrow \mathrm{(TBNO\text{-}BO)_3} + 6\,\mathrm{TBNA}$$

However, as neither H_2O nor TBNA were observed in the ^1H NMR spectrum, this is extremely unlikely, and is more probably due to other effects.

The melting points of the crude samples were also consistent with mixtures of products. The first crop of product did not begin to soften until 110°C, as would be expected from a composition of mainly the orthoborate (m. pt. 130-2°C), and the second crop softened at 88°C, the final solid residue not melting until 130°C, thus suggesting a much lower melting point for the metaborate. The slight bubbling and condensation of a clear liquid on the cooler parts of the melting point tube suggests the dehydration of boric acid. The analysis figures were also consistent with mixtures of ortho and metaborates, together with some other boron species (e.g. boric acid).

From the CH_2O peaks in the ^1H NMR spectra, it was possible to calculate the relative amounts of ortho and metaborates in the two crops of product from this reaction, both of which were completely soluble in $CDCl_3$:

Crop	Orthoborate (%)	Metaborate (%)
First	73	27
Second	11	89

Assuming that the percentage of unreacted boron species was small, this gave an approximately 2:3 ortho:meta ratio, with a yield of metaborate of 66%.

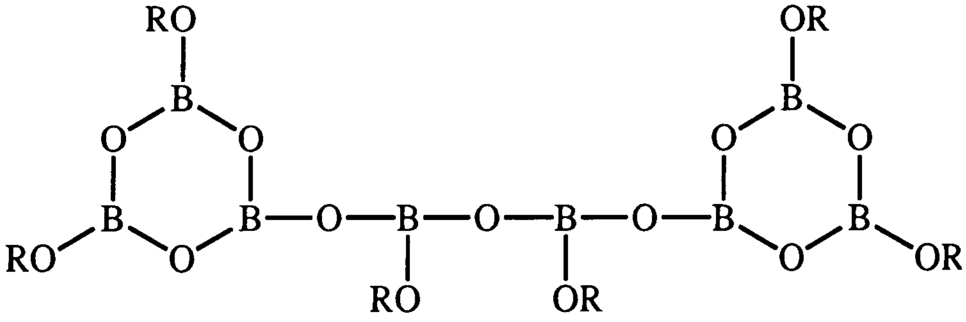
In the reaction with ground reactants and removal of solvent (section 2.4.2.a(iii)), distilling the reaction solution as near as possible to dryness seemed to have yielded mainly the expected metaborate species. The volume of water isolated was certainly consistent with this, although as mentioned before, any unreacted boric acid in refluxing toluene would be expected to dehydrate to produce the theoretical maximum amount of water (1.5 moles/mole acid). If the amount of water isolated was less than the theoretical maximum amount, this would have indicated that some TBNA remained unreacted. This was not shown by IR and NMR. Both the IR and NMR spectra indicated that the major product was the metaborate. The ^{1}H NMR spectrum also showed a small amount of orthoborate present in both crops of product. The original solid was redissolved in toluene in an attempt to separate any orthoborate, as in the larger scale preparations the metaborate seemed to be much more soluble in toluene, tending to remain in solution whereas the orthoborate formed tended to precipitate out on cooling. However, the integration of the CH_2O peaks in the ^{1}H NMR spectrum indicated that both crops of product contained similar proportions of orthoborate (19% in the first crop, 14% in the second).

Assuming that all the boron species reacted with TBNA to give either ortho or metaborate (which was reasonable, as the IR spectrum showed no signs of OH due to $B(OH)_3$/$(HOBO)_3$, and the solids completely melted by 140°C, ruling out B_2O_3), the yields of the two borates could be calculated from the ^{1}H NMR spectra (see over).

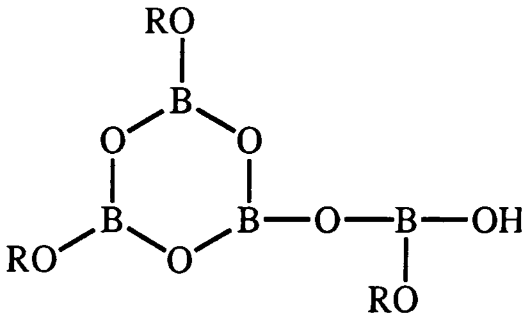
Crop	Orthoborate (%)	Metaborate (%)
First	19	81
Second	14	86

This gives an overall yield of metaborate of 77%.

A 1:3 ratio of boric acid:TBNA should produce the orthoborate, and a 1:1 ratio the metaborate. Using a greater than equimolar ratio raises the possibility of forming polyborate species. These are related to the metaborates, containing the same B_3O_6 ring system, but with the remaining boron valencies, caused by the deficiency of alkoxy groups, used to link the rings *via* B-O-B bridges. Thus, these polyborate species form a continuum between the discrete metaborates and the extended boric oxide matrix. For this reason, attempts at the preparation of polyborates usually yield mixtures of products. The 4:3 ratio used in section 2.4.2.b, however, has the possibility of producing a well defined, discrete, lower polyborate:



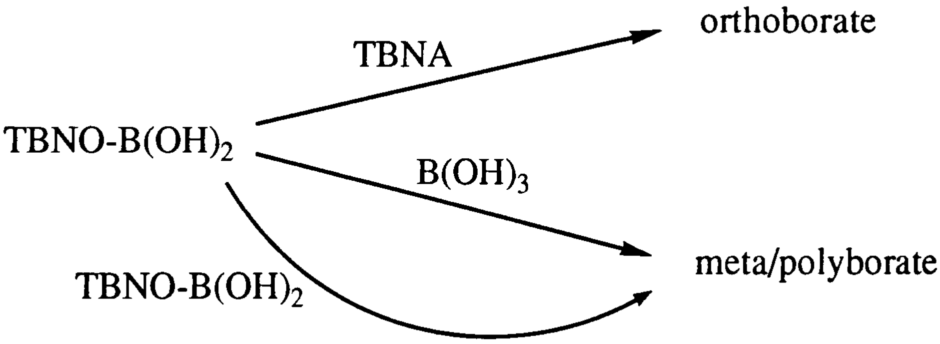
The other possible product:



would probably undergo self condensation under the conditions of the reaction to yield the first material.

The reaction conditions used appeared to yield orthoborate and metaborate, similarly to the 1:1 reactions already detailed. The IR spectra supported this conclusion, that of the first crop of product being an orthoborate spectrum also containing some OH bands ($B(OH)_3/(HOBO)_3$), and that of the second crop being metaborate which hydrolysed to the orthoborate on exposure to air. However, the NMR spectra did not appear to concur. Both of the ^1H NMR spectra had anomalous integration results, and showed several signals where only one would have been expected. The signals corresponding to CH_2Br were both much stronger than expected, and were shifted ~0.07-0.1ppm downfield from the usual position at 3.53ppm. The appearance of several signals in the CH_2O region in both the ^1H and ^{13}C spectra suggested that several different CH_2O environments were present in the products. The same applied to the CH_2Br signals in the ^1H and ^{13}C, and to the C signal in the ^{13}C spectra, though to a lesser extent, as these groups would be expected to be less affected by a change in the environment at the point of attachment than the CH_2O groups. The ^{11}B NMR spectra seemed to indicate a differing environment from both the ortho and metaborates (18.2ppm and 18.9ppm, respectively), but only a single environment nevertheless, whereas three would have been expected for the well defined 4:3 polyborate species.

One possibility is that the first stage of the reaction was the formation of a $TBNOB(OH)_2$ species. This could then react as below:



The species $(TBNO)_nB(OH)_{3-n}$ would tend to be less soluble in toluene (as boric acid is very insoluble and $B(OTBN)_3$ tends to precipitate out preferentially before the metaborate) and could have been isolated as the first crop of product. They would thus show an IR spectrum similar to the orthoborate, although also containing OH bands, but contain ^1H NMR signals due to the B-OH, which may very well appear in the CH_2Br region ($B(OH)_3$ has a signal at 2.97ppm in d_6-acetone, and substitution of TBNO groups may be expected to shift the remaining OH resonances downfield slightly).

The second crop of product would then consist of B-O-B-linked systems, i.e. metaborates, polyborates, which, although being more soluble in toluene, would still contain B-OH groups. This was supported by the amount of water isolated from the reaction, which was not a sufficient amount to indicate complete dehydration of all the boric acid used. Thus the B-OH resonance in the ^1H NMR spectrum may again have coincided with the CH_2Br signal, but would not be expected to be as strong as in the first crop, which was indeed observed. The IR spectrum would also be expected to show B_3O_6 ring bands, as in metaborate, which was again observed, although no strong OH bands were seen. The ^{11}B NMR signals may be due to the partially substituted $(TBNO)_nB(OH)_{3-n}$ species, and may possibly indicate an equilibrium in the d_6-acetone solution presenting an average signal. Both crops of product were insoluble in $CDCl_3$. This scheme would also explain the numerous different CH_2O ^1H NMR signals, as there would be several boron environments. The melting points of both crops of product were consistent with orthoborate-type units and metaborate-type units being the major constituents. However, as the second product remained cloudy, even up to 200°C, there may have been some material present containing an extended lattice. This may have been some sort of polyborate.

The reactions with a 2:1 ratio of $B(OH)_3$: TBNA were performed in an attempt to provide a system with an effective excess of boric acid. One of the major problems with this reaction was the tendency of the acid to aggregate in hot toluene, thus reducing the effective ratio of acid to alcohol.

These reactions (section 2.4.2.c) did not show any evidence of the formation of polyborates, as might have been expected from the stoichiometry used. On the contrary, the products seemed to be very well defined. The first crop of product, from IR and elemental analysis evidence, seemed most likely to be mainly metaboric acid, i.e. the product of the first stage of dehydration of boric acid. Some boric acid and boric oxide may also have been present (calculated boron analysis: boric acid, 17.48%; metaboric acid, 24.67%; boric oxide, 31.06%; observed, 22.55%). The ratio of C:Br in this product was 1.6:1, which corresponds to the TBNO group, and the ^1H NMR spectrum shows very weak signals due to the metaborate, the bulk of the solid remaining undissolved in $CDCl_3$, as would be expected for the three boron compounds mentioned above. The amount of metaborate in the first crop of product was ≤ 10% from the analysis obtained.

The second crop of product proved to be almost pure metaborate. The IR spectrum was very clear, and showed the expected hydrolysis on exposure to air to give the orthoborate. The ^1H NMR spectrum was that of the metaborate, with very few impurity peaks, even those due to the orthoborate, which was not present in any measurable quantity. The analysis of the crude product agreed very well with that expected for the metaborate. The amount of water isolated was consistent with the formation of metaborate and the partial dehydration of the excess boric acid (e.g. expect for incomplete dehydration of excess boric acid to metaboric acid 2.02ml, observed 1.90ml). The yield of metaborate isolated was 97%.

From the above reactions, and the earlier preparation of tribromoneopentyl orthoborate, it can be seen that the boric acid/TBNA system offers a convenient route to both the ortho- and metaborates, depending on the stoichiometry and conditions used. A 1:3 acid:alcohol ratio, or excess of alcohol, yields the orthoborate exclusively in good, even quantitative yields. The metaborate is more difficult to prepare in reasonable yield using this route, however, due to three main factors:

1) The physical state of the reactants
2) The dilution of the reactants in the solvent
3) The distillation conditions used

The reactions were, in effect, solid-solution reactions, the boric acid being insoluble in toluene, and the TBNA reasonably soluble, certainly in the amounts used. Thus, for most effective reaction of the boric acid, it needed to be in suspension as a fine powder. However, it had a tendency when suspended in toluene to aggregate and form lumps of solid, thus presenting a much smaller surface area for reaction. These lumps could to some extent be broken up by continued agitation of the solution by vigorous stirring, but often some lumps remained when heating was stopped. Also, some acid was unavoidably deposited on the sides of the flask by the boiling of the solution. This could be washed down to some extent by swirling the flask, but this could be counterproductive, as it also tended to deposit further solid. The aggregation and removal of the acid from the solution, both had the effect of reducing the effective acid:alcohol ratio, which would, of course, tend to lower the yield of metaborate and increase that of orthoborate.

The second point mentioned follows on from the first in that the greater quantity of reactants there are per unit volume of solvent, the more likely is aggregation to take place. Smaller amounts of boric acid were more easily dispersed and the alcohol more easily dissolved. The third point takes account of the fact that the longer the distillation was allowed to continue, the more water could be removed and the higher the yield of metaborate. This was effectively limited by the amount of solvent used and the temperature at which it was heated. Heating was generally continued until the distillate was clear at a still-head temperature of 110°C, which was taken to indicate that no more water was being removed. Continuing the distillation until only 10-20ml liquid remained in the flask provided a longer reaction time and also helped to wash down any water which was invariably deposited in the condenser.

Reactant Ratio	Boric Acid (g)	TBNA (g)	Yield Metaborate (%)
1:1	3.81	19.91	≤ 20
1:1	2.78	14.61	66
1:1	2.01	10.55	77
4:3	2.18	8.60	-
2:1	4.63	11.80	97

For the 1:1 reaction, it can be seen that the yield of metaborate increased as the factors mentioned above were optimised. The first two factors affected the effective acid:alcohol ratio, and the third the reaction time. The 4:3 reaction seemed to produce metaborate in a mixture of products, making it very difficult to give a figure for the yield. The 2:1 reaction overcame the problem of low effective acid:alcohol ratio by using an excess of acid, thus reducing the effects of aggregation. It is unclear why the 4:3 reaction should have yielded such a mixture of products rather than the ortho/metaborate mixture given by the 1:1 reactions, or even predominantly metaborate as in the 2:1 reaction. Ortho and metaborate certainly seem to have been present, but in the presence of other TBNO-containing species and another, acetone soluble, material which produced a ^{1}H NMR signal.

It can be concluded that the best method of preparing the metaborate is to use an excess of finely ground acid to alcohol, at high dilution in solvent, and distil until most of the solvent has been removed, or until the required amount of water has been removed. The solid produced can be recrystallised from hot toluene to give pure metaborate.

Properties of pure $(TBNOBO)_3$

Melting point: **144-5°C**

IR (nujol mull/KBr plates/prepared under nitrogen; cm^{-1}): **1505m, 1465s (broad), 1445s, 1415s (δCH), 1370s, 1350s (νBO), 1310s, 1285m, 1275m, 1270m, 1250m, 1230m, 1195w, 1190w, 1180w, 1150vw, 1095s (νCO), 1075m, 1060w, 1030w, 1020w, 930w, 900vw, 855m, 850m, 840m, 835w, 815m, 805w, 790w, 735m; 730s, 720s, 710m (B_3O_6 out-of-plane ring bend bands); 695w, 680w, 660w, 645w, 610m, 585w, 495vw, 480w, 470vw, 450w, 390vw.**

^{1}H NMR, δ: **3.55**s (CH_2Br), **4.07**s (CH_2O).

^{13}C NMR, δ: **34.0** (CH_2Br), **43.8** (C), **63.7** (CH_2O).

^{11}B NMR, δ: **18.9.**
(All in $CDCl_3$ solution).

Typical analysis (%):	B 3.09, C 17.79, H 2.29, Br 64.62.
Calculated for $(TBNOBO)_3$:	B 3.08, C 17.13, H 2.30, Br 68.36.

2.6.2 Borazine Derivatives

Two methods were used to synthesise N-triphenyl-B-trichloroborazine, $(PhNBCl)_3$ - both starting from boron trichloride and aniline. Firstly the adduct was formed, and this was then either treated with base to pull off HCl[21], thereby forming the borazine (section 2.5.2), or heated under reflux in toluene to drive off the HCl (section 2.5.1), the method used by Gerrard & Mooney[17]. The base method was tried first using DABCO, which produces a crystalline, readily separable HCl complex (white solid, section 2.5.2.a). However, the product prepared by this route was not obtained in as pure a state as that obtainable by the reflux method. Using triethylamine as the base caused problems of separation of the base.HCl complex from the final product, as was also found by Bartlett *et al.*[19]. As the reflux method was the most convenient practically, this was used for general preparations.

The IR spectrum of the adduct (section 2.5.1) was of interest in that it appeared to show *two* νNH stretching bands near 3200cm^{-1}, at 3220 & 3180cm^{-1}. Gerrard and Mooney report seeing only one band for this species[17], and a gap of 40cm^{-1} might be expected to have been readily separable by them. They use their result to postulate that the structure of the complex is that of the phenylaminoborondichloride hydrochloride type, not the classical coordination type on the basis of the IR evidence. The ^1H NMR spectrum of the borazine (sections 2.5.1 & 2.5.2) is not very informative due to the positions of the signals and the coupling of the protons. The expected spectrum from this system would be a doublet from the protons ortho to the nitrogen, a doublet of doublets from the meta protons, and a triplet from the para proton. The coupling constants $^3J_{ortho-meta}$ and $^3J_{meta-para}$ would be expected to be similar in magnitude as they are both between protons ortho to each other on a benzene ring. The $^4J_{ortho-para}$ would be expected to be so small as to be unobservable. However, the shifts of the various protons would also be expected to be similar, thus leading to a lot of overlap between the signals and a spectrum which is difficult to assign with any certainty.

The N-tris(4-bromophenyl)-B-trichloroborazine, $(pBrC_6H_4NBCl)_3$, was prepared using the reflux method (section 2.5.3). The material was not sufficiently soluble in the common NMR solvents to make the recording of these spectra worthwhile. The IR spectrum appeared to show that the material was reasonably hydrolytically stable, being unchanged on exposure to air for three hours. This may be due to the effect of the bromine atom on the phenyl ring deactivating the borazine ring to attack by water, although the increased electron withdrawing effect might be expected to have the reverse effect, increasing the likelihood of nucleophilic attack on the ring. The bromine would be too far removed from the borazine ring to have an appreciable steric effect. It could be that a canonical form of the structure with the bromine in the 4 position actually increases the electron density on the ring, thus making it more stable. It would be of interest to see whether the similar 3-bromo derivative would be *less* stable than the triphenyl derivative.

The synthesis of N-triphenyl-B-tris(3-bromo-2,2-bis(bromomethyl)-1-propoxy)borazine, $(PhNB\text{-}OTBN)_3$, via the LiOTBN method with elimination of LiCl was smooth (section 2.5.4). The recrystallised product gave clear NMR spectra which could be assigned with confidence, although the integration of the ^1H signals seemed to indicate more aromatic species than would be expected, and also showed evidence for the presence of toluene, even in the recrystallised, dried product. The major bands in the ^{13}C NMR spectrum could be assigned to $(PhNB\text{-}OTBN)_3$, but it was difficult to tell from the ^{13}C NMR spectrum whether the correct ratios of species were present. The ^1H NMR spectrum showed the CH_2Br, CH_2O and aromatic bands expected of the product, and frequently three other bands to the high frequency side of the other aliphatic signals. These decreased on increased reflux time, but not on recrystallisation. This may indicate that these peaks were due to one of the reactants, and that shorter reflux times were not sufficient to allow full substitution to take place, yielding low integration values for the aliphatic signals. From the analysis results, which were high in carbon and hydrogen, the compound appeared to crystallise as the toluene solvate. This could account for the toluene signals in the ^1H NMR spectra, and would also account for the high aromatic integration.

Similarly for N-tris(4-bromophenyl)-B-tris(3-bromo-2,2-bis(bromomethyl)-1-propoxy)borazine, $(p\text{-}BrC_6H_4NB\text{-}OTBN)_3$ (section 2.5.5), the NMR spectra could be assigned, but the elemental analysis was again high in carbon and hydrogen, showing signs that the compound crystallised as the toluene solvate. Gerrard *et al.* also found that this compound contained toluene on crystallisation[22].

2.7 References

1) JJ Ebelman & M Bouquet; Ann. Chem. Phys., 1846, 17, 54.

2) JJ Ebelman; Ann., 1846, 57, 331.

3) H Schiff; Ann. Suppl., 1867, 5, 154.

4) A Lamy; Ann. Chim., 1864, 3, 373.

5) W Gerrard & AH Woodhead; J. Chem. Soc., 1961, 519.

6) NM Cullinane & SJ Chard; Nature, 1949, 164, 710. NM Cullinane, SJ Chard, GF Price & BB Millward; J. Soc. Chem. Ind. London, 1950, 69, 538. (Chem. Abs. 1951, 45, 7950).

7) E Weiss, H Alsdorf & H Kuhr; Angew. Chem. Int. Ed. Eng., 1967, 6, 801. (Chem. Abs. 1967, 67, 120706).

8) PJ Wheatley; J. Chem. Soc., 1961, 4270.

9) RC Mehrotra; J. Indian Chem. Soc., 1953, 30, 585. VJ Shiner, D Whittaker & VP Fernandez; J. Am. Chem. Soc., 1963, 85, 2318. TN Huckerby, JG Oliver & IJ Worrall; J. Inorg. Nucl. Chem., Lett., 1969, 5, 749.

10) JG Oliver, PK Phillips & IJ Worrall; J. Inorg. Nucl. Chem., 1969, 31, 1609.

11) Dow Chemical Co., Neth. Appl., 6,601,266.

12) WJ Jackson & WR Darnell (Eastman Kodak Co.), US 3,763,644.

13) H Mayerhoeffer, W Mueller & U Sollberger (Sandoz Ltd.), Ger. Offen. 2,238,243.

14) e.g. BC Childress & RH Barker; J. Fire Retard. Chem., 1981, 8(2), 106-16; Proc. Int. Conf. Fire Saf., 1981, 6, 233-45; J. Fire Retard. Chem., 1981, 8(2), 65-81.

15) GA Burk & DN De Mott (Dow Chemical Co.), US 3,456,041.

16) TJ Swihart (Dow Corning Corp.), Ger. Offen. 2,736,068. PL Brown (Dow Corning Corp.), US 4,031,121.

17) W Gerrard & EF Mooney; J. Chem. Soc., 1960, 4028-36.

18) RG Jones & R Kinney; J. Am. Chem. Soc.,1939, 61, 1378-81.

19) RK Bartlett, HS Turner, RJ Warne, MA Young & IJ Lawrenson; J. Chem. Soc. (A), Inorg. Phys. Theor., 1966, 479-500.

20) H Noth & B Wrackmeyer, "NMR - Basic Principles and Progress. NMR Spectrometry of Boron Compounds", Vol. 14, Springer-Verlag, Berlin, 1978, p.192.

21) e.g. HS Turner & RJ Warne; Chem. & Ind., 1958, 526.

22) W Gerrard, EF Mooney & DE Pratt; J. Appl. Chem., 1963, 13, 127-33.

CHAPTER THREE

3 The Synthesis of Derivatives of 3-Bromo-2,2-bis(bromomethyl)-1-propanol - Silicon, Phosphorus, Titanium, Zinc, Aluminium and Magnesium Derivatives

3.1 The Preparation of Silicon Derivatives

3.1.1 The Preparation of Tetrakis(3-bromo-2,2-bis(bromomethyl)-1-propoxy)silane, $Si(OTBN)_4$.

3.1.1.a Method 1

In a typical preparation, 22.68g (69.8mmol) TBNA was weighed into a dry 250ml, two-necked, round-bottomed flask together with 4.0g (35mmol) diazobicyclooctane (DABCO) and a magnetic stir bar. The flask was then fitted with a gas inlet tap and a pressure-equalising dropping funnel sealed with a rubber septum. The apparatus was then evacuated and purged with dry nitrogen three times. The mixed solids were dissolved in 30ml dichloromethane and the solution cooled to -30±5°C before a solution of 1.0ml (8.7mmol) $SiCl_4$ in 10ml dichloromethane was added dropwise with stirring. This gave a white precipitate immediately, and on completion of addition the suspension was allowed to warm to room temperature and stirred for a further 15 minutes to ensure complete reaction. Filtration yielded a white solid and a clear, colourless solution. Removal of the solvent from this solution in vacuo gave a clear, very viscous colourless liquid which solidified on standing into fans of white solid.

First white solid:

Mass = 9.12g

Expect DABCO.2HCl = 35.0mmol = 6.50g, so 2.62g excess mass.

IR spectrum (nujol mull/KBr plates/prepared quickly in air), cm^{-1}: 3340w (νOH), ~2300s (v. broad, NH^+), 1165w, 1055s, 995w, 980m, 800w, 410m, plus other bands due to $Si(OTBN)_4$ (see the IR spectrum of the second white solid).

<u>Second white solid:</u>

Mass = 17.23g
Expect $Si(OTBN)_4$ = 17.5mmol = 23.16g (74% yield)

Melting point: 99-101°C

IR spectrum (nujol mull/KBr plates/prepared quickly in air), cm^{-1}: 1430m (δCH), 1320w, 1290m, 1275m, 1250m, 1230m, 1190w, 1155m, 1105s (Si-O-C), 1075m, 1035w, 910w, 870w, 860m, 840m, 820m, 805w, 785w, 765m, 660w, 610m, 540m (doublet), 480w.
From liquid film before crystallisation: 3010m, 2960s, 2890s, 2840w (νCH) & 1470s, 1430s, 1395m (δCH) (see page A-8).
No change after exposure to air for thirty minutes.

^1H NMR - solution in $CDCl_3$:

δ	Multiplicity	Assignment	Integration
3.53	s	CH_2Br	3.2
3.98	s	CH_2O	1.0

^{13}C NMR - solution in $CDCl_3$: δ: 34.0 (CH_2Br), 44.6 (C), 64.0 (CH_2O).

Elemental analysis: C 17.27, H 2.30, Br 66.53, 77.7(Octel analysis).
Calculated for $Si(OTBN)_4$: C 18.15, H 2.44, Br 72.45.

3.1.1.b Method 2

56.71g (175mmol) TBNA was weighed into a 1000ml, three necked, round bottomed flask with a large magnetic stir bar. The flask was then fitted with a gas inlet tap, a rubber septum and a pressure equalising dropping funnel sealed with a septum. The whole apparatus was then evacuated three times and purged with dry nitrogen. 200ml dry toluene was added to dissolve the TBNA, followed by 5.0ml (44mmol) $SiCl_4$ with stirring. No discernible reaction occurred. 25ml (179mmol, slight excess) triethylamine was added dropwise with stirring to the solution to give an exothermic reaction and a white precipitate. The solution was not cooled as the TBNA was not very soluble in toluene; the temperature of the reaction was controlled by a water bath and the rate of addition of the base. The reaction mixture was stirred for an hour after the completion of addition of base to ensure complete reaction. The suspension was filtered to give a white solid and a clear, colourless solution. Removal of the solvent from this solution in vacuo yielded a second white solid.

First white solid:

IR spectrum (nujol mull/KBr plates/prepared quickly in air), cm^{-1}: 2600s, 2490s (NH^+), 1400s, 1335w, 1290w*, 1275w*, 1250w*, 1175s, 1100m*, 1070m, 1035s, 890w*, 850m, 810m, 610w*, 465w*.
* Due to Si species. Otherwise, the spectrum is of Et_3NHCl.

This material was very sticky, presumably due to incomplete removal of solvent and some $Si(OTBN)_4$. Recrystallisation from DCM yielded a dry white solid:

IR spectrum (nujol mull/KBr plates/prepared quickly in air), as above, but, cm^{-1}: ~3410w (νOH), 2970s, 2930s (νCH), 2740s, 2670s, 2490s (NH^+), 1475s, 1440s, 1400s, 1390m, 1370w (δCH).

i.e. spectrum of Et_3NHCl.

^1H NMR - solution in $CDCl_3$:

δ	Multiplicity	J (Hz)	Integration
1.28	t	7.3	22.3
2.04	s	-	2.9
3.01	q	7.3	25.3
3.40	s	-	2.3
3.81	s	-	0.8

i.e the spectrum of Et_3NHCl with some $Si(OTBN)_4$ impurity.

Washing a 4.62g sample of the crude solid in water yielded 2.16g of insoluble residue (47%). Recrystallisation of this residue from DCM yielded a white crystalline material which showed the IR and NMR spectra of $Si(OTBN)_4$.

Recrystallisation of the crude solid from hot toluene also yielded $Si(OTBN)_4$.

Second white solid:

This showed the same analysis as the final product obtained by method 1, i.e. $Si(OTBN)_4$.

3.1.2 Preparation of (Phenoxy)(4-bromophenoxy)silanes, $Si(OC_6H_4Br)_n(OC_6H_5)_{4-n}$

In a typical preparation, 1-5g of $SiCl_4$ was vacuum transferred onto ~200ml frozen (liquid nitrogen) dry toluene and allowed to warm to room temperature to produce a solution of $SiCl_4$. To this was added a solution of phenol and triethylamine in toluene, dropwise, with stirring to yield a solution of $SiCl_n(OC_6H_5)_{4-n}$ and Et_3NHCl. After stirring for 30 minutes to allow completion of the reaction, a solution of 4-BrC_6H_4OH and triethylamine in toluene was added, dropwise with stirring. The resultant suspension was allowed to stir at room temperature overnight before being filtered to give a white precipitate of the DABCO.2HCl complex and a pale fawn solution. Removal of solvent from this solution in vacuo gave liquid products with varying viscosities and varying in colour from dark brown to pale fawn.

Reactants:

n	C_6H_5OH (mmol)	Et_3N (mmol)	$SiCl_4$ (mmol)	$pBrC_6H_4OH$ (mmol)	Et_3N (mmol)
0	36.5	37.3	9.1	-	-
1	78.6	78.9	26.0	26.0	28.7
2	15.0	17.9	7.5	15.0	17.9
3	7.8	8.6	7.8	23.5	24.4
4	-	-	8.2	33.0	35.2

Products:

n	Mass of base.HCl complex (g)	% of mass expected	Mass of product (g)	% yield
0	4.88	97	2.55	70
1	16.54	115	7.73	63
2	4.48	108	2.65	63
3	4.76	110	2.22	45
4	5.43	112	3.05	52

Liquid products:

IR spectrum (nujol mull/KBr plates/prepared quickly in air, the spectrum for the compound with n = 2), cm^{-1}: ~3050w (νCH, aromatic), 1595m, 1490s (δCH?), 1245s (broad, Si-O-C), 1170m, 1070m, 1030m, 1010s, 975s.br.,830m, 760m, 730w, 690m, 630w, 590w, 505m (see pages A-9 to A-11).
The spectra for the other compounds in the series were the same apart from the intensities of the bands at: $1595cm^{-1}$; 830, 760, $690cm^{-1}$; $1030cm^{-1}$.

^1H NMR spectra:

n = 4:

δ	Multiplicity	J (Hz)	Integration
6.86	d	8.8	69
7.32	d	8.8	67

Some residual $pBrC_6H_4OH$ peaks at: 6.68(d) & 7.28(d) were also present, the latter being partly hidden under the product signal. There were also some peaks due to aliphatic impurities.

n = 0:

The major signal in this spectrum was a multiplet at δ: 6.8-7.3, with major signals at δ: 7.10, 7.13, 7.23 & 7.26. This was due to the complicated coupling between the protons on the phenyl ring.

n = 1-3:

In these spectra, as n increased, the two doublets of the $pBrC_6H_4O$-group gradually became prominent over the multiplet of the C_6H_5O-group.

^{13}C NMR spectra:

n = 2:

δ	Assignment
115.7	C_4
119.4	C_2'
121.2	C_2
123.3	C_4'
129.7	C_3'
132.6	C_3
151.4	C_1
152.2	C_1'

N.B. C_{1-4} refer to phenoxy groups, C'_{1-4} refer to 4-bromophenoxy groups.

Again, as n increased from 0 to 4, the intensities of these signals varied, the intensity of the bands due to C_2 and C_3 decreasing, with the intensity of the bands due to C_2' and C_3' increasing.

3.1.3 Preparation of Methyl(3-bromo-2,2-bis(bromomethyl)-1-propoxy)silanes, ($Me_{4-n}Si(OTBN)_n$ (n = 1-3).

In a typical preparation, 15-25g TBNA was weighed into a clean, dry flask and dissolved in a suitable solvent (toluene or dichloromethane). To this solution was then added the required methyl silicon chloride, with stirring. This did not produce a reaction in any case. To the stirred solution was added, at room temperature, a solution of DABCO to give an exothermic reaction and a white precipitate. Overnight stirring at room temperature was found to be sufficient to complete the reaction, after which filtration yielded a white precipitate of the DABCO.2HCl complex and a clear, colourless solution. Removal of solvents from this solution under reduced pressure gave clear, colourless liquid products with viscosities increasing with n.

Reactants:

n	TBNA (mmol)	DABCO (mmol)	$Me_{4-n}SiCl_n$ (mmol)
1	79	39	79
2	33	16	16
3	51	26	17

Products:

n	DABCO.2HCl (g)	Yield (%)	Product (%)
1	13.6	189	72
2	3.0	102	84
3	7.4	104	90

Base complex:

IR spectrum (nujol mull/KBr plates/prepared quickly in air), cm^{-1}: ~3420w (νOH), 3000s (νCH), 2870s, 2770s, 2700s, 2560s, 2520s (NH^+), 2450s, 1450m (δCH), 1415m, 1390m, 1055s, 990w, 890w, 870w, 850w, 805w.

The spectrum is that of DABCO.2HCl. Unchanged on exposure to air for thirty minutes.

Liquid products:

IR spectra (thin film, prepared quickly in air), cm^{-1}:

n = 1:
3580w (νOH), 2960s, 2910m, 2870m (νCH), 1470s, 1430s (δCH), 1310w, 1275s, 1255s, 1230m, 1190w, 1100vs (Si-O-C), 1035m, 875vs, 840vs, 750s, 690m, 670m, 610m, 510w, 480w.
Unchanged on exposure to air for thirty minutes.

n = 2:
3580w (νOH), 3010w, 2960w, 2880w (νCH), 1610w (PhMe impurity), 1500w, 1470m, 1430s (δCH), 1310w, 1275s, 1250s, 1230w, 1190w, 1040vs (Si-O-C), 1035m, 880s, 860s, 840s, 785m, 730m, 695m, 670w, 610m, 530w, 480w, 470w (see page A-12).

n = 3:
3580w (νOH), 3020w, 2960w, 2880w (νCH), 1500w, 1470m, 1430s (δCH), 1310w, 1275s, 1250s, 1230w, 1190w, 1095vs (Si-O-C), 1035m, 880s, 860s, 840s, 785m, 730s, 695m, 670w, 610m, 530w, 480w, 470w.
On exposure to air, the spectrum remained unchanged, though the viscous liquid started to solidify. This was presumably due to evaporation of any remaining solvent and crystallisation rather than hydrolysis, as a re-melted sample showed the same thin film IR spectrum.

^{1}H NMR spectra:

n	δ			Integration		Calculated TBNO integration
	Me	CH_2Br	CH_2O	Me	TBNO	
1	0.08	3.44	3.53	1.0	0.9	0.9
2	0.17	3.44	3.68	1.0	2.4	2.7
3	0.28	3.52	3.84	1.0	7.0	8.0

^{13}C NMR spectra:

n	δ			
	Me	CH_2Br	C	CH_2O
1	-0.9	34.4	43.7	61.3
2	-3.6	34.3	43.9	61.6
3	-7.9	34.2	44.2	62.1

Analysis:

n = 1:	
	C 23.91, H 4.24, Br 59.45
Calculated:	C 24.20, H 4.32, Br 60.38
n = 2:	
	C 22.22, H 3.37, Br 61.77
Calculated:	C 20.42, H 3.14, Br 67.93
n = 3:	
	C 19.08, H 2.72, Br 67.83
Calculated:	C 18.94, H 2.68, Br 70.88

3.1.4 Preparation of Methyl(4-bromophenoxy)silanes, $Me_{4-n}Si(OC_6H_4Br)_n$ (n = 1-3).

3.1.4.a Method 1

In a typical preparation, a solution of 2.0ml (16.5mmol) Me_2SiCl_2 in 15ml dry toluene was made up in a clean, dry flask under dry nitrogen. To the stirred solution was added, dropwise with stirring at room temperature, a solution of 5.65g (32.7mmol) p-bromophenol in 20ml dry toluene. This gave no noticeable reaction, and the solution was refluxed for five hours and allowed to cool. Removal of the solvent under reduced pressure yielded a fawn, slightly viscous liquid.

3.1.4.b Method 2

In a typical preparation, 8.57g (49.5mmol) p-bromophenol and 2.79g (24.8mmol) DABCO were weighed into a clean, dry flask under dry nitrogen and dissolved in 100ml dichloromethane to give a pale fawn solution. Addition of 3.0ml (24.8mmol) Me_2SiCl_2, dropwise with stirring at room temperature, gave an exothermic reaction which produced a white precipitate. After stirring for one hour, filtration yielded a white precipitate of DABCO.2HCl which was washed through with 2 x 10ml dichloromethane, and a clear, colourless solution. Removal of solvents from this solution under reduced pressure gave a slightly viscous fawn liquid.

Reactants:

Silicon chloride	Chloride (mmol)	DABCO (mmol)	p-bromophenol (mmol)
Me_3SiCl	39.4	19.7	39.4
Me_2SiCl_2	24.8	24.8	49.5
$MeSiCl_3$	25.5	38.3	76.7

Products:

n	DABCO.2HCl		Product	
	mass (g)	% yield	mass (g)	% yield
1	4.63	115	7.56	78
2	4.35	95	8.90	89
3	7.35	104	12.13	85

<u>Liquid products (methods 1 & 2):</u>

IR spectra (thin film, prepared quickly in air), cm^{-1}:

n = 1:
~3420w (broad, νOH), ~3070vw (νCH, aromatic), 2570w (νCH, methyl), 1590m (aromatic ring), 1490s, 1430w (δCH), 1270s, 1260s (C-O-Si), 1170w, 1095w, 1070w, 1010w, 915s, 845s, 830s, 760w, 725w, 700vw, 600w, 495w.

n = 2:
3520w, 3360m (broad, νOH), ~3060vw (νCH, aromatic), 2960w (νCH, methyl), 1590m (aromatic ring), 1490s, 1430w (δCH), 1350w, 1260s (Si-O-C), 1170m, 1090m, 1070s, 1010m, 920m, 860w, 820s, 805s, 730w, 605w, 500m.

n = 3:
~3560w (νOH), ~3080vw (νCH, aromatic), 2980w (νCH, methyl), 1590m (aromatic ring), 1490s, 1430w (δCH), 1405w, 1280s, 1250s (Si-O-C), 1170m, 1110m, 1095m, 1070m, 1010m, 960s, 830s, 800s, 785m, 740w, 700w, 630w, 600w, 570w, 500m.

^{1}H NMR spectra:

n	$\delta_{aromatic}$		J (Hz)	$\Delta\delta$	δ_{Me}
	2 position	3 position			
1	6.74	7.32	8.8	0.58	0.53
2	6.82	7.33	8.7	0.51	0.26
3	6.87	7.35	8.6	0.48	0.26
4	6.86	7.32	8.8	0.46	-

3.2 Preparation of Phosphorus Derivatives

3.2.1 Preparation of Tris(3-bromo-2,2-bis(bromomethyl)-1-propyl) phosphite, P(OTBN)$_3$ from Phosphorus Trichloride and (3-bromo-2,2-bis(bromomethyl)-1-propoxy)lithium, LiOTBN.

13.01g (40mmol) TBNA was weighed into a dry 250ml, 2-necked, round-bottomed flask together with a magnetic stirrer bar. The flask was then fitted with a gas inlet tap and a pressure equalising dropping funnel sealed with a rubber septum before being evacuated and purged with dry nitrogen three times. 40ml dry toluene was added via the funnel to dissolve the TBNA. 25.0ml (@ 1.6M, 40mmol) butyl lithium in hexanes was then added slowly, dropwise, with stirring at 0-5°C to yield a white suspension of LiOTBN which was allowed to warm to room temperature and stirred for 15 minutes. to ensure complete reaction. A solution of 1.0ml (11.5mmol) PCl_3 in 5ml dry toluene was then added dropwise to the stirred suspension to give an exothermic reaction. On completion of addition, the mixture was stirred for 15 minutes. at room temperature before being refluxed for 15 hours. The resultant suspension was allowed to cool to room temperature and filtered to give a white solid and a clear, colourless solution. Removal of solvents from this solution in vacuo yielded a cloudy viscous liquid which, on standing, solidified to give a soft white solid.

White solid:

Mass = 3.05g.
(Expect LiCl = 34.5mmol = 1.46g)
Also excess LiOTBN = 1.82g
Total = 3.28g

IR spectrum (nujol mull/KBr plates/prepared under nitrogen), cm^{-1}: This is the same as that of the viscous liquid product, but much weaker.

NMR Spectra (^1H, ^{13}C & ^{31}P in $CDCl_3$): These are also the same as those of the viscous liquid product, but required ten times as many scans to produce comparable spectra.

Viscous liquid:

Melting point = 87-89°C (lit. 88°C[1])

IR spectrum (Thin film/KBr plates/prepared quickly in air), cm^{-1}: 3580w (OH?), 3020, 2960, 2880 (νCH), 1275m, 1245m, 1040m, 1010s (νPOC), 850m, 815m, 770m.
IR of solid (Nujol mull/KBr plates/prepared under nitrogen), cm^{-1}: 3300vw (broad, OH), 1430s (νCH), two groups centred on 1270s & 1240s, 1075, 1040, 1010vs (νPOC), 850, 820, 805, 770s, 610s (see page A-13).

^{1}H NMR (solution in $CDCl_3$).

δ	Multiplicity	Assignment	J (Hz)	Integration
3.47	s	CH_2Br	-	3
3.88	d	CH_2O	4.8	1

^{13}C NMR (solution in $CDCl_3$).

δ	Multiplicity	Assignment	J (Hz)
33.9	s	CH_2Br	-
43.8	d	C	5.0
61.6	d	CH_2O	10.3

The signals at 33.9 & 61.6ppm both had a weak higher frequency companion, the shifts of which corresponded exactly to those of TBNA.

^{31}P NMR (solution in $CDCl_3$).
This showed only one major signal, at 138.8ppm, split into a septet (J = 4.8Hz), and two much weaker peaks at 7.7 & -3.4ppm.

3.2.2 Preparation of Tris(3-bromo-2,2-bis(bromomethyl)-1-propyl) phosphate, $P(O)(OTBN)_3$

3.2.2.a From Phosphorus (V) Oxychloride, $POCl_3$, and LiOTBN

13.92g (43mmol) TBNA was weighed into a clean, dry flask and dried by evacuating the sealed flask at 50°C for 15 minutes and then purging three times with dry nitrogen. The TBNA was dissolved in 50ml toluene and 27.0ml (@ 1.6M, 43mmol) butyl lithium in hexanes was added, dropwise with stirring at room temperature, to give a suspension of LiOTBN in an exothermic reaction. The temperature was controlled to <40°C by the rate of addition of the butyl lithium and a cold water bath. The suspension was stirred for fifteen minutes to ensure the completion of the reaction. A solution of 1.0ml (11mmol) $POCl_3$ in 5ml toluene was then added, dropwise with stirring at room temperature, to give an exothermic reaction and more white solid (the suspension became noticeably thicker). On completion of the addition, the stirred suspension was heated to reflux for 16 hours. The suspension was allowed to cool to room temperature and filtered to yield a white solid and a clear, colourless solution. The solid could be purified by recrystallisation from dichloromethane.

White solid:

Mass = 10.59g
Expect from the reaction: 10.93g $P(O)(OTBN)_3$, 1.40g LiCl & 3.31g excess LiOTBN. Total mass expected = 15.64g, so 68% yield of solid.

IR spectrum (nujol mull/KBr plates/prepared under nitrogen), cm^{-1}: 1430m (δCH), 1310w, 1295m, 1280m, 1260m, 1245s, 1230m, 1190w, 1080m, 1050m, 1035vs, 910m, 850m, 830w, 820w, 790w, 725w, 705w, 665w, 610m, 570m, 485m, 460w.
After exposure to air, strong sharp OH bands appear at 3390 & $1635cm^{-1}$, indicative of water absorbed by LiCl.

^1H NMR spectrum:

δ	Multiplicity	Assignment	J (Hz)	Integration
3.54	s	CH_2Br	-	3
4.23	d	CH_2O	3.7	1

^{31}P NMR spectrum:
One signal at -2.8ppm, which is split into a septet in the ^1H-coupled spectrum, with a coupling constant of 3.7Hz. This indicates ^{31}P-^1H coupling with a magnitude consistent with P-O-C-H, i.e. ^3J.

The ^1H NMR spectrum shows the presence of TBNO groups, but no free alcohol. The splitting of the CH_2O signal is due to the coupling with P, as shown by the coupling constant.

3.2.2.b From Phosphorus (V) Chloride, PCl_5, and TBNA

2.21g (10.6mmol) PCl_5 was weighed into a clean, dry flask under dry nitrogen, together with 17.27g (53mmol, 5 x PCl_5) TBNA. The flask was then evacuated for fifteen minutes at 50°C before being purged with dry nitrogen three times. 60ml dry toluene was then added at once, with stirring, to produce an immediate effervesence, liberating a colourless gas. The TBNA dissolved in the toluene, leaving some solid, presumably PCl_5, in suspension. On continued stirring, a white precipitate began to appear, and after an hour this was allowed to settle. Bubbles of gas were still appearing, so the suspension was stirred overnight at room temperature. Evolution of gas had ceased after this, and the suspension was filtered to produce a white solid which was dried *in vacuo*.

White solid:

Mass 5.84g

Melting point: 158-60°C (lit. 172-3°C[2])

IR spectrum (KBr disc prepared in air), cm^{-1}: ~3400vw (νOH), 3010, 2960 (νCH), 1465, 1445, 1430, 1395 (δCH), 1310, 1295, 1280, 1260, 1250, 1230, 1080, 1045s (P-O-C?), 915m, 850m (see page A-14).

The spectrum was unchanged on exposure to air, apart from a slight increase in the OH band due to the absorption of water. The OH band could be removed completely by recrystallisation from CH_2Cl_2. Also on recrystallisation, the P-O-C band at $1045cm^{-1}$ was resolved into a doublet at 1050 & $1040cm^{-1}$.

The solid was insoluble in toluene, acetone, diethyl ether and water, but soluble in CH_2Cl_2 and $CDCl_3$.

^1H NMR spectrum:

δ	Multiplicity	Assignment	J (Hz)	Integration
3.55	s	CH_2Br	-	4
4.23	d	CH_2O	3.7	1

^{13}C NMR spectrum:

δ	Multiplicity	Assignment	J (Hz)
33.9	d	CH_2Br	5.2
44.4	d	C	8.8
67.9	d	CH_2O	5.2

^{31}P NMR spectrum (see page A-15):

One signal at -3.1ppm, shows splitting into a septet with J = 3.7Hz.

Mass spectrum (see pages A-16 & A-17): EI^+: m/e = 343, 324, 307, 263, 245, 214, 183, 165, 133, 119, 101, 65, 53.
CI^+: m/e = 263, 214, 149, 133, 97, 83, 69, 53.
CI^-: m/e = 160, 79.

3.3 Preparation of Derivatives of Other Metals and Metalloids

3.3.1 Preparation of Titanium tetrakis(3-bromo-2,2-bis(bromomethyl)-1-propoxide, $Ti(OTBN)_4$, from $TiCl_4$.

3.3.1.a Method 1

To a cooled, stirred (-30°C, dry ice/acetone) solution of 11.85g (36.5mmol) TBNA and 2.06g (18.2mmol) diazobicyclooctane (DABCO) in 20ml dichloromethane was added a solution of 1.0ml (9.1mmol) $TiCl_4$ in 20ml dichloromethane, dropwise with stirring. There was an immediate reaction which yielded a yellow precipitate. On warming to room temperature this precipitate became white. Filtration yielded a white solid. Removal of solvents from the resultant colourless solution yielded a viscous, colourless liquid.

White solid:

Mass = 6.95g.
Expect DABCO.2HCl = 3.37g

IR spectrum (nujol mull/KBr plates/prepared under nitrogen), cm^{-1}: The spectrum was that of DABCO.2HCl with some TiOC-containing material also present.

Viscous liquid:

IR spectrum (thin film/KBr plates/prepared quickly in air): 3580w (νOH), 3020w, 2960w, 2920w, 2860w (νCH), 1465w, 1430m, 1370w (δCH), 1270m, 1240m, 1095vs (broad, Ti-O-C?), 1030w, 860w, 840m, 815w, 740s, 710s, 660w, 610w (see page A-18).
This spectrum showed signs of hydrolysis even with only brief exposure to the atmosphere. On prolonged exposure, the spectrum reverted to that of TBNA and the liquid solidified on the plates.

^{1}H NMR spectrum, δ (integration): 3.49 (3), 4.33 (1,broad), 5.28.
The first two signals were assignable to CH_2Br and CH_2O respectively.

^{13}C NMR spectrum, δ: 34.5vs (CH_2Br), 45.4m (C), 45.8w, 53.1vw, 54.3w, 74.9w (broad, CH_2O).

3.3.1.b Method 2

To a solution of 14.22g (43.8mmol) TBNA and 6.2ml (44.5mmol) triethylamine in 100ml dry toluene was added at room temperature, slowly, dropwise with stirring, a solution of 1.0ml (9.1mmol) $TiCl_4$ in 10ml toluene (on the addition of the $TiCl_4$ to the toluene, the solution became a deep red in colour). This gave an immediate exothermic reaction which produced a yellow precipitate in a yellow solution. The temperature of the suspension was controlled by the use of a water bath and by varying the rate of addition of the $TiCl_4$ solution. On completion of addition and further stirring, the suspension darkened in colour to a gold/brown. This was refluxed overnight to yield, on filtration, a white solid and a red/brown solution. Concentration of this solution yielded a viscous red/brown liquid, which appeared to be the product. However, an attempt to distil this liquid yielded only a clear, mobile liquid which proved to be toluene (IR spectrum), and a sticky solid brown residue. Dissolution of this residue in dichloromethane gave a clear, brown solution which, on concentration and cooling, yielded fawn crystals. The supernatant solution was syringed from these crystals, which were then washed with 3 x 2ml cold (-30°C) dichloromethane before being dried in vacuo to give a fawn solid.

White solid:

Mass = 7.62g
Expect Et_3NHCl: = 36.5mmol = 5.02g
So 152% obtained.

IR spectrum (nujol mull/KBr plates/prepared under nitrogen), cm^{-1}: 2740s, 2680s, 2610s, 2530m, 2500s (NH^+), 1445s, 1430s, 1400s, 1370m, 1190w, 1175s, 1070w, 1040s, 850m, 810m, 475w, 465w. i.e. the spectrum of Et_3NHCl. This spectrum is unchanged on exposure to air for 15 minutes.

Viscous red/brown liquid:

IR spectrum (thin film/KBr plates/prepared quickly in air), cm^{-1}: 3580w (vOH), 3030w, 2960w, 2920w, 2870w (vCH), 1610w*, 1500w*, 1465m, 1430m, 1380w*, 1305w, 1290m, 1275m, 1245m, 1180w, ~1100vs (broad, Ti-O-C), 1030m*, 860m, 840m, 815m, 800m, 755m, 730s*, 710s, 695s*, 670m, 640m, 610m, 510w, 480w, 470w*.
* Assignable to toluene.

After exposure to air: 3580w , 3340s, 3260s (vOH), 3030w, 2970w, 2890w (vCH), 1620vw (OH?), 1465m, 1430s, 1370w (CH), 1310m, 1285m, 1275m, 1240m, 1180w, 1130m,br, 1050s, 1020s, 920w, 855m, 840s, ~650s (broad, obscures bands).

This spectrum shows the hydrolysis of the Ti-O-C product back to TBNA.

Clear, mobile liquid:

The IR spectrum identified this material as toluene.

Fawn solid:

Mass = 7.97g
Expect Ti(OTBN)$_4$ = 9.1mmol = 12.22g

Melting point: melts 84-5°C

IR spectrum (nujol mull/KBr plates/prepared in nitrogen) cm^{-1}: 1430s (δCH), 1290m, 1275m, 1240m, 1085s (broad), 1030m (CO?), 860w, 840s, 815w, 755m, 720s (M-O?), 635w, 605m, 510w, 480w. After exposure to air, detail is lost and OH bands appear, the spectrum eventually reverting to that of TBNA.

^{1}H NMR spectrum:
Signals appeared at δ: 3.51s (CH_2Br), 3.63s, 4.42s (CH_2O) & 5.31s.

^{13}C NMR spectrum:
Signals were seen at δ: 33.5, 33.9, 44.0, 44.4, 44.8, 45.6, 75.3. These signals were grouped into three areas, assignable to CH_2Br, C & CH_2O respectively.

Analysis:	C 19.15, H 2.57, Br 74.61, Ti, 5.03
Calculated for Ti(OTBN)$_4$:	C 17.88, H 2.40, Br 71.38, Ti 3.57
Calculated for Ti$_2$(OTBN)$_6$:	C 17.67, H 2.37, Br 70.55, Ti 4.70

3.3.2 Attempted Preparation of bis(3-bromo-2,2-bis(bromomethyl)-1-propoxy)zinc (II), $Zn(OTBN)_2$

3.3.2.a From Dimethylzinc, Me_2Zn

2.57g (26.9mmol) Me_2Zn were vacuum distilled onto 20ml frozen dry toluene and warmed to 0°C to produce a solution of Me_2Zn in toluene. To this stirred solution was added a solution of 17.49g (53.9mmol) TBNA in 50ml dry toluene, dropwise at 0°C. On addition, effervescence occurred, evolving a colourless gas, and after a few minutes a white precipitate began to appear. After stirring overnight at room temperature, the white solid was separated by filtration and dried *in vacuo* to give a white powder.

White powder:

Mass = 7.21g
Expect $Zn(OTBN)_2$ = 26.9mmol = 19.8g.

Melting point: first change at 65-9°C (TBNA melting?), first liquid at 88°C, clear liquid at 135°C.

IR spectrum (nujol mull/KBr plates/prepared under nitrogen), cm^{-1}: 3220w (broad, νOH), 1430s (δCH), 1310w, 1270s, 1250s, 1225m, 1185w, 1160w, 1055vs, 1020s, 920w, 860m, 840s, 815m, 785w, 770w, 730w, 690m, 660s, 610m, 565s, 480m, 450m, 390w (see page A-19).
After exposure to air, the spectrum reverts to that of TBNA.

^1H NMR spectrum:
Signals at δ: 1.77s, 2.20s, 3.54s, 3.75s.

^{13}C NMR spectrum:
Signals at δ: 34.4 (CH_2Br), 44.1 (C), 62.5.(CH_2O)

Analysis: Zn 10.19, C 16.42, H 2.46, Br 60.83
Calculated for Zn(OTBN)$_2$: Zn 9.17, C 16.84, H 2.26, Br 67.24

3.3.2.b From diethylzinc, Et$_2$Zn

To a solution of 8.40g (26mmol) TBNA in 50ml dry toluene was added dropwise with stirring at room temperature a solution of 11mmol (10ml @ 1.1M in toluene) Et$_2$Zn. An immediate exothermic reaction evolved a colourless gas and slowly precipitated a white solid. After stirring overnight at room temperature, the white solid was filtered off.

White solid:

Mass = 4.43g
Expect Zn(OTBN)$_2$ = 11mmol = 7.84g

Melting point: 105-110°C.

IR spectrum (nujol mull/KBr plates/prepared under nitrogen), cm^{-1}: 1430m (δCH), 1315w, 1275m, 1250m, 1225vw, 1215vw, 1190w, 1100vw, 1060s, 1020m (CO?), 935m, 880w, 860m, 835m, 815w, 690w, 660m, 610w, 565m, 480w, 455m.
After exposure to air: 3560m, 3460m, 3340m, 3240m (νOH), 1620w (δCH), 1435m, 1430m, 1420w, 1310w, 1290m, 1275m, 1240m, 1230w, 1215vw, 1185vw, 1170vw, 1145vw, 1100w, 1060m, 1050m, 1020m, 990w, 920w, 875w, 865m, 855m, 840m, 825w, 815w, 770w, 690m, 660m, 620m, 610m, 535w.
i.e. the spectrum is that of TBNA.

^{1}H NMR spectrum:
The material was not very soluble in the common NMR solvents, but gave signals at δ: 3.54s & 3.75s.

^{13}C NMR spectrum:
Signals were observed at δ: 34.5 (CH$_2$Br), 44.3 (C) & 62.6 (CH$_2$O).

Analysis (crude): Zn 7.98, C 17.98, H 2.23, Br 62.88
Calculated for $Zn(OTBN)_2$: Zn 9.17, C 16.84, H 2.26, Br 67.24

3.3.3 Reaction of TBNA with triethyl aluminium, $AlEt_3$

To a stirred solution of 2.0ml (15mmol) Et_3Al in 20ml dry toluene was added dropwise with stirring at room temperature a solution of 14.25g (45mmol) TBNA in 40ml toluene. This produced a slightly exothermic reaction and the evolution of a colourless gas. By the completion of addition, a white precipitate had started to appear, so the solution was stirred overnight, then concentrated before being filtered to give a white precipitate and a clear, colourless solution. On standing, a second white solid crystallised out of this solution.

White precipitate:

Melting point: melts 200-20°C.

IR spectrum (nujol mull/KBr plates/prepared under nitrogen), cm^{-1}: 1425s, 1415m (δCH), 1310w, 1285m, 1270s, 1250m, 1225w, 1180m, 1140s (broad), 1075vw, 1045w, 1035m, 1000m, 940w, 900w, 860m, 840s, 815s, 780w, 735s, 685w, 670s, 650w, 605s, 530w, 490m, 480m (see page A-20).

^1H NMR spectrum:
Signals at δ (integration): 3.54s (190) & 3.76s (63).

^{13}C NMR spectrum:
Signals at δ: 34.4, 44.1, 62.5.

Analysis: Al 2.79, C 17.41, H 2.42, Br 64.47
Calculated for $Al(OTBN)_3$: Al 2.70, C 18.04, H 2.42, Br 72.02

Second white solid:

Melting point: 180-94°C

IR spectrum (nujol mull/KBr plates/prepared under nitrogen), cm^{-1}: 2740w, 1425s, 1410m (δCH), 1310w, 1285s, 1275s, 1250s, 1230m, 1185s, 1140s (broad), 1050s, 1015m, 900s, 855s, 840s, 810s, 800s, 775s, 750s, 690w, 675w, 650m, 610s (doublet), 560m, 525w, 480m, 450m.
After exposure to air for one hour, the spectrum remained unchanged apart from νOH bands at 3660w, 3350m & 3240m.

^{1}H NMR spectrum:
Signals at δ: 1.42t (J = 7.1Hz), 3.48s, 3.54s, 3.76m, 3.81s, 3.85s, 4.03m (J = 7.1 & 10.6Hz).

3.3.4 Reaction of Magnesium with TBNA

0.50g (21mmol) Mg turnings were placed in a clean, dry flask under nitrogen purge together with 13.37g (41mmol) TBNA. 40ml dry toluene was added to dissolve the TBNA and the mixture stirred at room temperature. Addition of a few small I_2 crystals failed to produce a reaction in the still solution, so the stirred suspension was refluxed overnight. Immediately on reflux a white precipitate began to appear. After overnight reaction, the suspension was allowed to cool and filtered to give a white solid which was dried *in vacuo*.

White solid product:

Melting point: softens ~150°C, melting complete at 190°C.

^{1}H NMR spectrum:
Signals at δ: 3.56s & 3.79d.

The material was sparingly soluble in the NMR solvents, so the spectrum seen could be that of residual TBNA.

Analysis: Mg 2.90, C 15.87, H 2.55, Br, 68.49
Calculated for $Mg(OTBN)_2$: Mg 3.62, C 17.87, H 2.40, Br 71.34

3.4 Discussion

3.4.1 Silicon Derivatives

The two methods used to produce $Si(OTBN)_4$ (section 3.1.1) were used on differing scales; method 1 (section 3.1.1.a) for smaller scale work, the base complex being easy to separate from the product, and method 2 (section 3.1.1.b) for larger scale sample preparation. The latter method utilised the hydrolytic stability of the product in its separation stages, the crude solid being washed with water and the insoluble residue recrystallised from, e.g. dichloromethane, to yield pure $Si(OTBN)_4$. Clean ^1H & ^{13}C NMR spectra were obtained, clearly showing the reacted TBNO groups. The elemental analysis obtained was satisfactory for $Si(OTBN)_4$, though the usual problems occurred with the bromine analysis.

The phenoxy-type species (section 3.1.2) were all liquids, so would be of little use in a flame retardant role, but showed some interesting trends in their spectra. The variation of the four bands with n in the IR spectra could be used to assign the bands to the responsible group. Their intensities relative to adjacent, unchanged bands could be calculated and plotted as a function of n.

n	1595cm^{-1}	1030cm^{-1}	830cm^{-1}	690cm^{-1}
0	0.96	0.88	0.25	0.93
1	0.84	0.77	0.67	0.81
2	0.62	0.57	1.02	0.71
3	0.48	0.35	1.52	0.42
4	0.45	0.00	1.65	0.09

Notes: 1595cm^{-1} band measured relative to 1490cm^{-1} band,
1030cm^{-1} relative to 970cm^{-1}, and 830 & 690cm^{-1} relative to 760cm^{-1}.

(1) The 1595cm^{-1} band was due to a C-C aromatic ring stretch. The diminishing intensity with n was presumably due to the absorption in p-bromophenoxy- being weaker than in the phenoxy- group.

(2) The 1030cm^{-1} band may be ascribed to an in-plane aromatic C-H bend which appeared to be solely due to the C_6H_5O- group and not shown by p-BrC_6H_4O-, as the intensity dropped to zero for n = 4. This could be explained if the absorption was mainly due to the para hydrogen.

(3) The bands at 830 & 690cm^{-1} could be assigned to an out-of-plane aromatic C-H bend, due to the pBrC_6H_4O- and C_6H_5O- groups respectively. This would account for their complementary change in intensities with n.

Similarly, the change in intensities of the proton NMR signals allowed them to assigned to specific carbon atoms on the two groups, the two doublets due to 4-bromophenoxy clearly increasing in intensity over the complex multiplet due to phenoxy as n increased.

The IR spectra of the methyl silane derivatives of TBNA (section 3.1.3) did not show the expected smooth variation in intensity of the methyl CH band, although the intensity did vary with n. The proton NMR spectra did, however, show good agreement with the theoretical values for the integration ratios of methyl to TBNO protons, and the elemental analyses were also in good agreement with theory. All of the compounds were again liquids, so of little use as flame retardants.

The methyl silane derivatives of 4-bromophenol (section 3.1.4) were also of some interest as a series of compounds, though again of little use in flame retardant applications. The proton spectra were of especial interest, due to the behaviour of the aromatic signals. The methyl signal did not appear to fall regularly from 0.53ppm for n = 1 to zero at n = 4 (NMR standard, tetramethylsilane, TMS), though it did drop to 0.26ppm for n = 2 & 3. The aromatic signals, on the other hand, did vary regularly with n. The resonance due to the protons in the 3 position on the ring stayed more or less constant with n at ~7.33ppm, but that due to the protons at the 2 position increased in frequency from 6.74 to 6.86ppm, the rate of change decreasing as n increased. This is clearly shown by the $\Delta\delta$ figure in the NMR table of results. This was presumably due to the proximity of the protons at the 2 position to the silicon atom with its varying degree of methyl substitution. The 3 position protons, being further removed from this site, would be expected to be affected less by the substitution at silicon.

3.4.2 Phosphorus Derivatives

The slight excess mass obtained for the LiCl obtained in section 3.2.1 seemed to indicate that some of the expected product was conatined in it.

This was borne out by the fact that NMR spectra (^1H, ^{13}C & ^{31}P) were obtainable, and showed the same signals as those of the viscous liquid product, though requiring ten times as many scans to produce comparable signal strengths. As LiCl and LiOTBN are both insoluble in $CDCl_3$, the excess mass can be put down to the phosphite. The IR spectrum of the solid product was also very weak, as would be expected from a sample mainly consisting of LiCl.

The viscous liquid product, the phosphite, showed strong bands in the IR due to the νPOC vibration. The NMR spectra were also clear and readily interpretable. The proton spectrum showed only the two signals expected of the TBNO- group and were assignable by their integrals and relative positions, though being shifted to higher frequency relative to TBNA. The ^{13}C spectrum also indicated that the alcohol had reacted, the shifts for the carbons being shifted from their positions in TBNA. The weak impurity signals corresponded exactly to those of TBNA, either unreacted or possibly a product of slight hydrolysis. The ^{31}P NMR signal showed that the compound was pure, only one signal being seen, with two very slight impurities. The resonance at 138.8ppm was consistent with a phosphite species[3], the splitting indicating the presence of $P(OTBN)_3$. The impurities at 7.7 & -3.4ppm may possibly have been due to small amount of phophoryl species, $P(O)(OR)_nCl_{3-n}$, formed by partial reaction of the phosphorus trichloride with the TBNA followed by oxidation.

The products of section 3.2.2, the phosphate, also showed good NMR spectra. The proton NMR clearly showed the TBNO groups, with no free TBNA present, and the peaks could be assigned on the basis of their integrals. The CH_2O signal was also split into a doublet by the phosphorus, the magnitude of the coupling constant (3.7Hz) consistent with ${}^3J_{P-O-C-H}$. This was also shown by the ${}^{31}P$ NMR spectrum, which showed a single signal split into a septet. The chemical shift of ~-3ppm was consistent with a phosphate, $PO(OR)_3$. The splitting of the signal into a septet indicated that the phosphorus was coupling to six equivalent protons, thus indicating that a $P(OTBN)_3$ grouping was present. The ${}^{13}C$ spectrum was also very clear and readily assignable, the signals also showing splitting into doublets by ${}^{31}P$. The reverse splitting of the ${}^{31}P$ signal by ${}^{13}C$ was not seen due to the low natural abundance of ${}^{13}C$.

The EI+ mass spectrum shows the characteristic fragmentation pattern of TBNO (major peaks at m/e = 214, 133, 53). Peaks at m/e = 324 & 343 are also present. These correspond to TBNA (molecular ion) and 3-bromo-2,2-bis(bromomethyl)-1-chloropropane, TBNCl, respectively. As the TBNA was used in excess, it may be expected to appear on the mass spectrum, though the fact that it came out of solution into the product is surprising. Also, it was not detected by NMR, so it could possibly have formed by slight hydrolysis. TBN-Cl could have been formed by:

$$PCl_5 + TBNA \longrightarrow POCl_3 + TBN\text{-}Cl + HCl$$

thus leaving $POCl_3$ and 4 TBNA, which could react:

$$POCl_3 + 3\,TBNA \longrightarrow P(O)(OTBN)_3 + 3\,HCl$$

So, overall:

$$PCl_5 + 5\,TBNA \longrightarrow P(O)(OTBN)_3 + TBN\text{-}Cl + TBNA + 4\,HCl$$

The $PO(OTBN)_3$ would appear as the fragmentation pattern of the TBNO- group, which is the same as that of TBNA, minus the molecular ion peak. The bulk of the TBNA would remain in solution in toluene, possibly along with the TBN-Cl, though small amounts seem to have been included with the phosphate, as shown by the mass spectra.

CI^+:

This spectrum shows the fragmentation pattern of TBNO-, plus a signal at m/e = 263, which is consistent with the loss of HBr from TBN-Cl.

CI^-:

Major peaks appear at m/e = 160 & 79 and show isotope peaks consistent with Br_2 and Br-containing residues respectively:

Signal	Observed intensity	Calculated intensity
157.88	100	100
159.88	192	195
161.88	92	96
78.95	100	100
80.96	96	98

The evidence shown seemed to suggest that the product formed was the phosphate, $P(O)(OTBN)_3$. However, the IR spectrum was interesting in that it did not show a strong absorption characteristic of P=O, as one would expect from $P(=O)(OTBN)_3$ The other possible product of the reaction with phosphorus pentachloride to contain the $P(OTBN)_3$ grouping as indicated by the ^{31}P NMR spectrum would be $P(OTBN)_3Cl_2$. This could either exist as the five coordinate phophorane or the phosphonium chloride. The latter would contain free chloride ion, and this was not shown by a chloride test using silver nitrate. The chlorine atoms in the phosphorane structure would be expected to be reactive towards atmospheric moisture, and yet the phosphate products from both section 3.2.2.a and 3.2.2.b were indefinitely stable in air. It thus appeared that the material was indeed the desired phosphate, $P(O)(OTBN)_3$, showing only a weak P=O absorption in the IR.

3.4.3 Derivatives of Other Metals and Metalloids

The IR spectrum of the viscous liquid product is section 3.3.1.a showed only weak signals in the OH region of the spectrum, indicating that free TBNA was not present, and also showed a strong signal assignable to TiOC at $1095cm^{-1}$. The proton NMR spectrum supported this view, with two signals attributable to the CH_2O and CH_2Br groups of the TBNO unit, the CH_2O signal being broadened by its proximity to the titanium atom. Similarly, the CH_2O carbon signal in the ^{13}C NMR spectrum was also broadened and shifted a long way from the TBNA resonance of 62ppm.

The viscous red/brown liquid obtained in section 3.3.1.b also showed the strong TiOC band in the IR spectrum, and its purification by recrystallisation from dichloromethane to yield the fawn solid also showed this signal. The compound appeared to be highly sensitive to moisture, however, eventually reverting to TBNA, as easily observed by the IR spectrum. However, the compound did not give a good elemental analysis for $Ti(OTBN)_4$, suggesting perhaps a mixture of species. The ^1H & ^{13}C NMR spectra showed the same behaviour as seen with the product in section 3.3.1.a, the two weaker signals in the proton spectrum possibly representing bridging TBNO units, which would help to account for the anomolous elemental analysis.

The white solid product of section 3.3.2.a showed a strong signal in its IR spectrum at 1055cm^{-1} which could be assignable to the ZnOC group, but also showed little hydrolytic stability. The ^{13}C NMR spectrum showed little change from the spectrum of TBNA, especially noticeable for the CH_2O peak at 62.5ppm. This may be due to the low solubility of the material in the NMR solvent, so the spectra recorded are actually those of the TBNA formed by hydrolysis of the zinc compound. The elemental analysis was in reasonable agreement with that calculated for $Zn(OTBN)_2$. The product obtained using diethylzinc in place of dimethylzinc (section 3.3.2.b) would seem to be a purer sample of this compound, having a sharper melting point. The IR spectrum showed the same ZnOC band, but also showed the same instability in air.

The first product of TBNA and triethylaluminium (section 3.3.3) appeared to be a high melting solid with reasonable hydrolytic stability, and also gave quite a good elemental analysis; possibly a promising potential flame retardant species. The second crop of product from this reaction appeared to show evidence in the proton NMR for residual ethyl goups (triplet at 1.42ppm). Both showed a strong IR band at 1140cm^{-1} attributable to AlOC, and no OH band due to free TBNA

The proton NMR of the magnesium compound (section 3.3.4) showed no evidence for the presence of free OH in the product, suggesting that the magnesium had indeed reacted through the OH group and not attacked one of the bromine atoms. However, the material was sparingly soluble in the NMR solvent, and this spectrum may not have been indicative of the bulk of the solid.

3.5 References

1) GA Burk & DN De Mott (Dow Chemical Co.), US 3,456,041
2) C Moore (Dow Chemical Co.), French patent 1,556,439.
3) e.g. DEC Corbridge, "Phosphorus - an Outline of its Chemistry, Biochemistry and Technology", Elsevier, Amsterdam, 1990.

CHAPTER FOUR

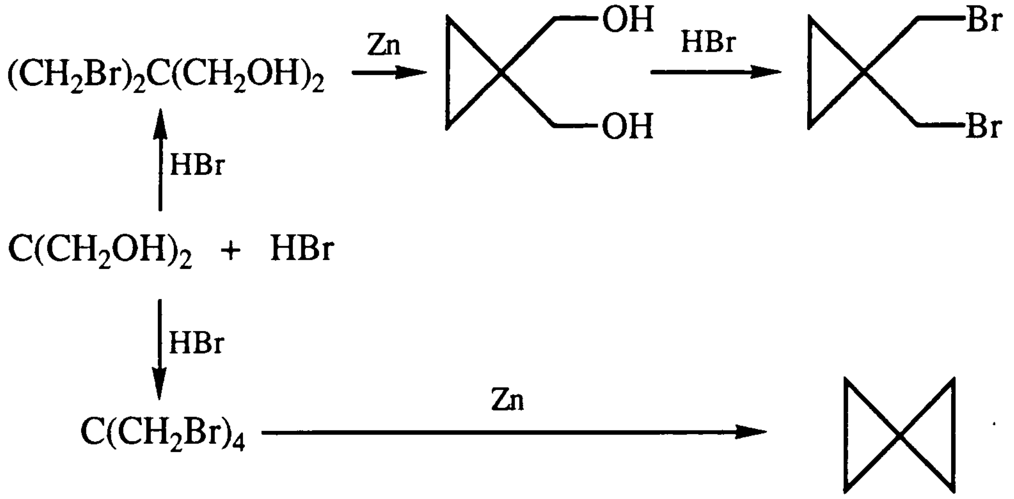
4 The Synthesis of Derivatives of 2,2-Bis(bromomethyl)-1,3-propanediol

4.1 Introduction and Historical Background

Dibromoneopentanediol (2,2-bis(bromomethyl)-1,3-propanediol, DBND) and tribromoneopentylalcohol (2,2-bis(bromomethyl)-3-bromo-1-propanol, TBNA) are both prepared by the same route, by the treatment of pentaerythritol with HBr:

$$C(CH_2OH)_2 + HBr \longrightarrow (CH_2Br)_nC(CH_2OH)_{4-n}$$

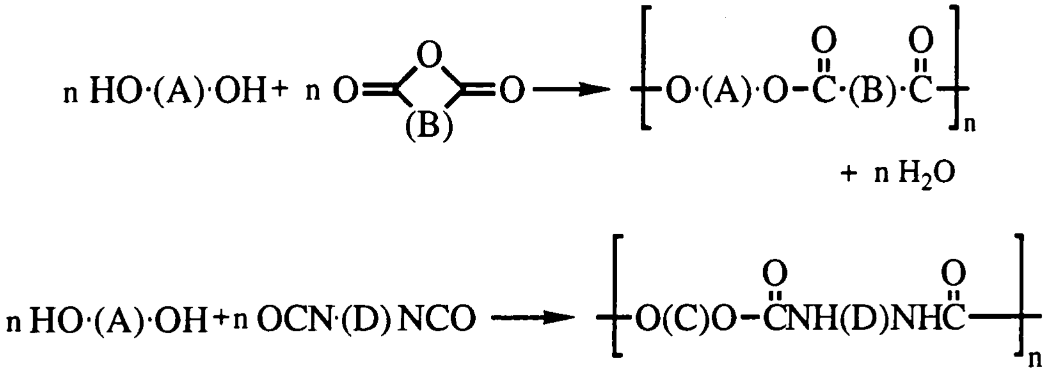
Thus, the histories of the two compounds are inextricably linked. The first references to the preparation of DBND and TBNA appeared almost a century ago in work involving the bromination of pentaerythritol as a route to "Spirocyclan" (spiropentane)[1,2,3,4]:



Some years later, in the late 1930's, brominated aliphatic nitrites were found to produce long lasting and predictable lowering of the blood pressure in humans[5], and during the 1950's the compounds $(CH_2Br)_nC(CH_2OH)_{4-n}$ were tested for such activity. The dibromo compound (n = 2, DBND) was found to be the most effective and least toxic, and was suggested as a drug for the treatment of such conditions as *Angina Pectoris* [6].

By the early 1960's, the use of synthetic high polymers had become widespread, and some of the problems of such a large scale use had become apparent. One of the major problems, particularly in such areas as textiles, was and is their flammability, so methods of reducing this were sought. The early 1960's saw the first use of DBND in flame retardant (FR) applications, with the synthesis of halogenated phosphates for use as additives in poly(methylmethacrylate)[7]. These new phosphate esters were found to be an improvement over those already in use as they were effective at a lower loading in the polymer (measured in parts per hundred resin, phr), thus leading to better retention of the physical properties of the polymer. Research was also being carried out on halogenated polyesters for use in applications where good solvent resistance was important. This led to the use of DBND as the diol in polyester and polyurethane synthesis, where its importance as a source of bromine atoms was quickly recognised.

As a difunctional molecule, DBND lent itself to use in polymerisation reactions:



Where (A), (B) & (D) are divalent organic groups, such as $(CH_2)_n$.

However, the polymers formed from DBND tended to have quite short chain lengths, due to the electron-withdrawing effect of the two bromomethyl groups making the hydroxyl functions less reactive toward the acid groups[8]. Thus, polymers formed using DBND as the only dihydroxy species had poor physical characteristics due to their short chain length compared to the non-halogenated polymer. There were two ways to overcome this problem. Firstly, it was possible to prepare a polymer using mainly a non-halogenated diol, but also incorporating sufficient DBND to produce the desired percentage of bromine in the end product. Due to its lower reactivity, the DBND units would tend to concentrate towards the end of the polymer chain, reducing the effect of the low reactivity. This had the disadvantage that it sometimes gave a coloured product[9], so a second method was more generally used. This involved preparing the non-halogenated base polymer as normal, but also preparing a polymer using only DBND, the two then being melt blended together in the correct proportions to produce the requisite percentage of bromine in the finished product.

One flame retardant on the market which uses this technique is known as FR1540 (CAS: 59025-78-4)[10]. It is a copolymer of DBND with isophthalic acid (1,2-benzenedicarboxylic acid), (E)-2-butenedioic acid and (Z)-2-butenedioic acid, and is used to blend with other polyesters to produce a flame retardant effect. It also has the advantage that it is unsaturated, so it can be cross-linked, with e.g. styrene, to produce a more rigid polymer. Such brominated systems are sometimes used with MoO_3 to reduce smoke production on burning[11].

The other major use of DBND is still in phosphorus-containing systems, mainly phosphate esters, phosphonates and phosphites[12]. These are generally prepared from P-Cl compounds such as PCl_3 or $POCl_3$, and are used as additive flame retardants in a variety of polymer systems. The problem of additive leaching out of the system over time can be overcome in some systems by the incorporation of the bromo species into the polymer backbone by converting it into an active phosphorus-containing polyol flame retardant:

$$\mathrm{HO{-}(A)_{Br}{-}O{-}[P]{-}O{-}(A)_{Br}{-}OH}$$

Where $(A)_{Br}$ is a divalent brominated organic group such as DBN & [P] is tri or pentavalent P.

The phosphorus and bromine work synergistically as flame retardants, the bromine acting solely in the vapour phase by interfering with the oxidation of the fuel produced by thermal degradation of the polymer[13] The phosphorus acts mainly in the solid phase by increasing the aromatic component of the residue[14]. It can also hinder chain scission, thus preventing the formation of volatile fuel components[15].

Sb_2O_3 is another synergist sometimes used with DBND, but it is not as effective as MoO_3 at reducing smoke production[16]. DBND has also been used in combination with zinc nitrate hexahydrate as a treatment for textiles[17], and with $CaCO_3$ as a replacement for $Al(OH)_3$ in polyester blends used for spray coating[18]. Boron has also been used in combination with DBND in the form of borate salts[19]:

$$B(OH)_3 + \text{excess DBND} \xrightarrow[M = R_4N]{MeOH/MOH} MB(ODBNO)_2$$

or as boric acid esters with TBNA[20].

Reactions with phosphonitrilic chloride trimer, $(NPCl_2)_3$, have also been reported[21], but not in terms of use as a flame retardant. The product is a mixture of six species, mainly containing chelating ODBNO units, but with some linking units. No studies involving the reaction of DBND with silicon reagents or $NaBH_4$ have been reported.

Many examples of main group alkoxides have been prepared using the tribromoneopentyl alcohol (TBNA) as a starting material, as described earlier. The dihydroxy analogue, dibromoneopentanediol (DBND) was thought to be useful due to its similar steric properties, which may provide hydrolytic stability, and its difunctionality, which could be used for linking alkoxylated main group units together with a brominated backbone. Thus simple alkoxides, which are often liquids, may be linked into chains, raising the molecular weight and the melting point.

The DBND could react in two ways to form rings or chains, depending on the metal residue involved:

1) $2\,M + HO\text{–}DBN\text{–}OH \longrightarrow M\text{—}O\text{–}DBN\text{–}O\text{—}M$

2) 

$M + HO\text{–}DBN\text{–}OH \longrightarrow M(O)_2DBN$

It was of interest to see which route the DBND preferentially took with certain reactive main group compounds, and what factors influenced the reaction route.

Three types of reaction were considered:

a) with reactive M-Cl
- i) alone
- ii) with base
- iii) with LiOR

b) with acidic M-O-H

c) with hydridic M-H

The present work presents the synthesis of some novel silicon derivatives of DBND by various routes, the preparation of a sodium borate from DBND and $NaBH_4$, and the preparation of a discrete boric acid ester containing only DBND with no TBNA.

4.2 Experimental

All manipulations carried out under dry nitrogen using standard Schlenk techniques or in a glove box, unless otherwise specified.

4.2.1 Reaction of DBND with Chlorosilanes

Attempted Preparation of Bis(tris(3-bromo-2,2-bis(bromomethyl)-1-propoxy)silicon)-2,2-bis(bromomethyl)-1,3-propandioxide, $(TBNO)_3Si$-(ODBNO)-$Si(OTBN)_3$

6.81g (6.6mmol) $(TBNO)_3SiCl$ (viscous liquid, pre-prepared by reacting $SiCl_4$ with three moles of TBNA in DCM with DABCO to remove the HCl formed) was dissolved in 30ml dry THF and a solution of 0.86g (3.3mmol) DBND in 10ml THF was added dropwise with stirring at room temperature. There was no noticeable effervescence or exotherm, but the colour of the solution faded from fawn to straw. The solution was stirred for three days before the solvents were removed in vacuo to give a viscous fawn liquid, from which slowly crystallised a white solid.

Viscous fawn liquid:

The IR spectrum showed it to be the starting material, $(TBNO)_3SiCl$.

White solid:

The IR spectrum was that of DBND.

4.2.2 Reaction of DBND and tetrachlorosilane, $SiCl_4$, in the presence of base

Attempted Preparation of $(TBNO)_3Si$-(ODBNO)-$Si(OTBN)_3$ from $SiCl_4$ and the Alcohols

5.28g (31.1mmol) $SiCl_4$ was vacuum transferred onto 100ml dry toluene. To the stirred solution was added, dropwise at room temperature, a solution of 30.29g (93.2mmol) TBNA and 13.0ml (93.2mmol) triethylamine in 70ml toluene. The TBNA had previously been vacuum dried and nitrogen purged three times and the dissolution with triethylamine was exothermic. This gave an exothermic reaction and a white precipitate. After allowing the suspension to cool to room temperature, a solution of 4.07g (15.5mmol) DBND and 6.3ml (45.2mmol, 40% excess) triethylamine in 70ml toluene was likewise added to give a slight exotherm and further white solid. (Note: the DBND was only slightly soluble in toluene, the triethylamine aided dissolution and would not interfere with the reaction. The excess could also be easily removed in vacuo later.) After cooling, the suspension was stirred for one hour before being filtered to give a white powder and a clear solution. Removal of solvent from the solution *in vacuo* gives a very sticky white resin. Hydrolysis of this resin in warm aqueous base for 12 hours yielded a white crystalline material.

White powder:

Mass = 20.57g, expect 17.12g.

The IR spectrum shows no OH but strong NH^+ bands, consistent with
Et_3NHCl.

This product contained some material which was insoluble in water but soluble in acetone. Hydrolysis of this material overnight in warm aqueous base yielded the same white crystalline product as hydrolysis of the resin described below.

Sticky white resin:

IR spectrum (cm^{-1}): 3600 (w,sharp - OH?); ~3100 (C-H arom., PhMe?); ~3000 (νCH aliph.); 1400-1500 (CH); 1250-1300 (due to TBN group); 1100 (strong, Si-O-C , as there is little chance of Si-O-Si in anhydrous conditions); 850-900cm (Si-O).
After exposure to air, a broad νOH band appears at ~3350cm, but with little change to the rest of the spectrum, even after one week (bands due to residual PhMe decrease in intensity).

^1H NMR, δ: 1.38 (t), 2.3 (s), 3.08 (mult.), 3.52, 3.93, 6.37 (weak, broad) & 7.1 (mult.).
Integration: δ: 2.3:δ 7.1 ≈ 3:5
δ 1.38:δ 3.08 ≈ 3:2.
δ 3.5:δ 3.9 ≈ 2.7:1.0.

^{13}C NMR, δ: 33.7, 44.1 & 63.0.

White crystalline material:

0.67g white crystals.

The IR spectrum was that of TBNA.

4.2.3 Attempted preparation of poly[bis(3-bromo-2,2-bis(bromomethyl)-1-propoxy)mono(2,2-bis(bromomethyl)-1,3-propandioxy)-silane], $[(TBNO)_2(ODBNO)Si]_n$

1.32g (7.8mmol) $SiCl_4$ was vacuum transferred onto 100ml dry toluene and a solution of 2.04g (7.8mmol) DBND & 5.0ml (35.9mmol) triethylamine in 50ml toluene was added dropwise with stirring at room temperature to give a mildly exothermic reaction and a white precipitate. The suspension was warmed to ~50°C with stirring, then allowed to cool before a solution of 5.05g (15.5mmol) TBNA & 2.5ml (17.9mmol) triethylamine was added dropwise with stirring to give an exothermic reaction and more white precipitate. The suspension was left to stir for 12 hours and then filtered to yield a white solid and a clear, colourless solution. Removal of toluene from this solution *in vacuo* gave a very sticky white resin.

White solid:

Mass = 4.57g.
Expect Et_3NHCl 31.2mmol = 4.29g (107%).

IR spectrum (nujol mull/KBr plates/prepared under nitrogen), cm^{-1}: major bands @ 2610 & 2500 (NH^+), bands at 1400, 1175, 1075, 1040, 850 & 810 due to Et_3NHCl. Broadening of bands ~1100 & ~870 indicates the presence of some Si-O-C species.

Sticky white resin:

IR spectrum (thin film/KBr plates/prepared quickly in air), cm^{-1}: 3590 (w, sharp, OH?); 2950m (doublet) & 2890m (sharp, CH stretch); 1470s & 1430s (CH bend); 1280s & 1250s (CO stretch?); 1100vs (broad, SiO stretch); 880m, 860m & 845m.

^1H NMR: Signals due to toluene appear @ δ: 2.28 & 7.11. Also, those due to Et_3NHCl appear @ δ: 1.04(t), 2.61(q) & 6.21(NH^+).

d	Strength	Integration
3.44	vs	135 together
3.45	vs	
3.61	w	8
3.84	m	48 together
3.86	m	
4.07	w	8

^{13}C NMR: Peaks present due to toluene.

δ	Strength	Assignment
33.3	w	
33.8	vs	CH_2Br
34.4	m	
44.0	m	C
61.9	w	
62.4	w	CH_2O
63.0	m	

On standing in air, the resin solidified to form a tacky grey gum.

4.2.4 Reaction of Chlorosilanes with Dilithium (2,2-bis(bromomethyl)-1,3-propandioxide), LiODBNOLi

Preparation of Silicon bis(2,2-bis(bromomethyl)-1,3-propandioxide), $Si(ODBNO)_2$, from tetrachlorosilane, $SiCl_4$, and LiODBNOLi

3.84g (14.7mmol) DBND was suspended in 150ml dry toluene and 18.4ml (@ 1.6M, 29.4mmol) BuLi in hexanes was added dropwise with stirring at room temperature to give an exothermic reaction and a white precipitate. This suspension was stirred for an hour and a solution of 1.21g (7.1mmol) $SiCl_4$ in 100ml toluene was added with stirring at room temperature. There was no noticeable reaction. The suspension was heated under reflux for 18 hours then allowed to cool. Filtration yielded a white solid and a clear fawn solution. Removal of toluene from this solution yielded a sticky fawn resin. On standing under nitrogen this resin set into a hard, fawn solid.

White solid:

Mass = 1.82g.
Expect LiCl, 28.4mmol ($SiCl_4$ limiting), 1.20g (152%).

IR spectrum (nujol mull/KBr plates/prepared under nitrogen), cm^{-1}: No detail at all; very slight OH @ 3300 & weak bands in the C-O/Si-O region (~1100). After exposure to air, bands appear @ 3430vs (νOH) & 1635s (OH), together with a broad absorption beginning @ ~1000 and going down to ~600 (40% transmission).

Sticky fawn resin:

IR spectrum (thin film/KBr plates/prepared quickly in air), cm^{-1}: 3500 vw (νOH); 2960, 2930 & 2880s (aliphatic νCH); 1470w & 1430w (CH); 1265w & 1250w; ~1100vs (broad, Si-O-C); 850s.
After exposure to air, the bands are broadened, detail is lost, and an νOH band appears @ 3350 vs.

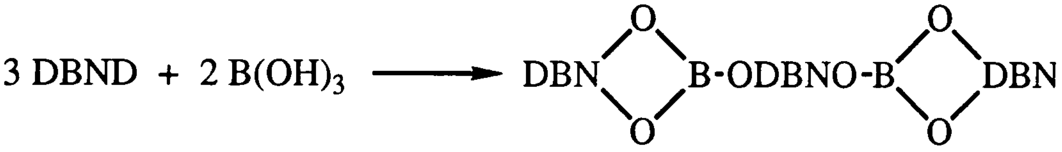
4.2.5 Reaction of DBND with acidic boric acid, $B(OH)_3$, in organic solvent

Preparation of trisdioldiborate from DBND and $B(OH)_3$ in toluene

13.58g (51.8mmol) DBND were placed in a 250ml, two-necked, round-bottomed flask together with 2.14g (34.6mmol) $B(OH)_3$. The flask was sealed and the contents dried in vacuo for one hour at room temperature before being purged with dry nitrogen three times. The mixture was then suspended in 100ml dry toluene and a distillation apparatus fitted to the flask and purged with nitrogen. This was wrapped in aluminium foil to minimise heat loss and aid distillation.

The stirred suspension was heated with an oil bath at atmospheric pressure. By 80°C, dissolution of the DBND was complete, leaving the boric acid in suspension. This tended to form lumps of solid even when finely powdered acid was used, and these stuck to the side of the flask and were quite slow to react. Boiling began at ~100°C and the first fraction distilled over at 84°C. Droplets of water were visible at the still head and in the condenser. The second fraction distilled over at 110°C as a cloudy liquid, presumably due to collection of water from the condenser. Distillation was continued until the distillate was clear; at this point ~50ml solution remained in the reaction flask. After cooling to room temperature, the reaction flask was removed and the stillhead and condenser repeatedly washed through with the distilled toluene to remove any remaining water. 1.73ml water were collected, with a small amount remaining in the apparatus.

For the reaction:



Expect 103.6mmol water = 1.87g = 1.87ml.

So, 93% of the expected yield of water was obtained, indicating a nearly quantitative reaction.

Removal of solvents from the reaction solution yielded a viscous fawn resin.

<u>Viscous fawn resin:</u>

IR spectrum (thin film/KBr plates/prepared quickly in air), cm^{-1}: 2960w, 2910w (aliphatic CH stretch), 1485s, 1420s (CH bend), 1345s (ν_aBO), 1265m, 1165m (CO stretch), 1065w (ν_sBO) (see page A-21).

Also bands at 3030, 1605, 730 & 690cm^{-1} due to toluene.

After exposure to air for 15 minutes, a weak, broad band appeared at 3460cm^{-1}, but the rest of the spectrum was unchanged.

^{1}H NMR

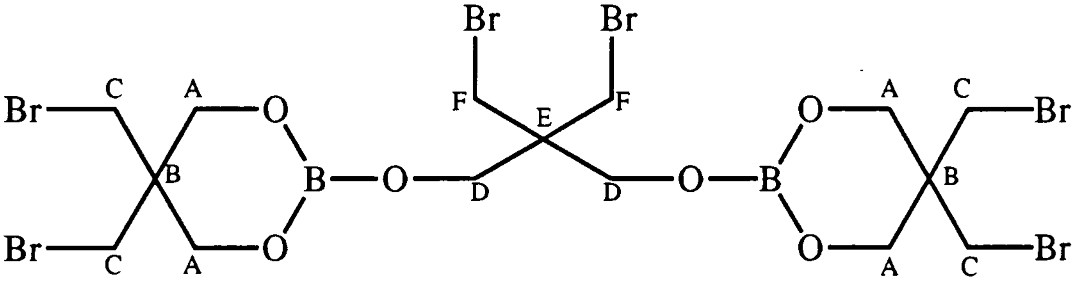
Signals due to toluene at δ: 2.31 (s), ~7.2 (multiplet)

δ	Multiplicity	Assignment	Integral	Ratio
3.42	s	C, F	116	3.1
3.81	2	D	37	1.0
3.92	s	A	79	2.1

^{13}C NMR

δ	Assignment	DBND to compare
33.7	C	36.0
34.1	F	"
39.1	B	45.2
43.7	E	"
62.4	D	62.0
66.8	A	"

Peaks were assigned on the basis of signal strength and shift from the DBND position.



4.2.6 Reaction of DBND with Sodium Tetrahydridoborate, $NaBH_4$

1.73g (46mmol) $NaBH_4$ was suspended in 50ml dry THF. To the stirred suspsension was added with stirring , at room temperature, a few drops of a solution of 24.00g (92mmol) DBND in 60ml THF until reaction started (gas evolution/effervescence). The first reaction of these two reagents had not been quite as cautious, and had resulted in a vigorous reaction and the distribution of a white product throughout the reaction system and associated gas lines. The suspension was then cooled to 5°C and the DBND solution added at such a rate as to sustain the reaction at a controllable rate (~5 bubbles/sec through the gas exhaust bubbler). After the completion of addition, the solution was warmed to 40°C and stirred until gas evolution ceased. The resultant cloudy solution was filtered at room temperature to yield a small amount of white solid and a clear, colourless solution. Removal of solvent from this solution yielded a white solid which was dried *in vacuo* at 50°C for five hours.

White powder:

Mass = 0.56g

IR spectrum (nujol mull/KBr plates/prepared under nitrogen), cm^{-1}: 2430w, 2330s, 2260m, 1265s, 1120vs.
This spectrum appeared to be essentially that of $NaBH_4$.
After fifteen minutes exposure to air, an OH band appeared at ~$3250cm^{-1}$.

White precipitate:

Mass = 24.92g

M. Pt.: 174-80°C to give an opaque white liquid.

IR spectrum (nujol mull/KBr plates/prepared under nitrogen), cm^{-1}: ~3280w (vOH), 1430m (CH), 1290w, 1250vs (B^--O?), 1215w, 1200vw, 1100vs (broad, C-O?), with shoulder at ~1050, 990vs, 965vs, 930vs, 910m, 860s, 830s, 675m, 660m (C-Br?) (see page A-22).
After exposure to air for one hour a sharp band appears at $3590cm^{-1}$, together with a broad band which peaks at 3360 & $3180cm^{-1}$. Otherwise, the spectrum is largely unaffected.

^{1}H NMR spectrum:

The solid was insoluble in $CDCl_3$, and sparingly soluble in acetone-d_6.

δ	Intensity	Multiplicity
3.56	w	s
3.61	w	s
3.63	s	s
3.66	m	s
1.79	w	m
2.06	w	m

Analysis (crude material): Na 3.81, C 24.64, H 3.52, B 1.88, Br 52.38

Expected for $NaB(ODBNO)_2$: Na 4.15, C 21.69, H 2.91, B 1.95, Br 57.73

Due to the insolubility of this material, it was impossible to get ^{11}B or ^{13}C NMR spectra.

4.3 Discussion and Conclusions

The attempted reaction of DBND with $(TBNO)_3SiCl$ produced only the starting materials, indicating that the residual chlorine atom on $(TBNO)_3SiCl$ is reasonably stable. The excess mass obtained with the base complex formed in the $SiCl_4$/TBNA/DBND reaction (section 4.2.2) can be accounted for by SiOTBN-containing products being filtered off with the Et_3NHCl. The IR spectrum of the sticky white resinous product was very similar to that of tetrakis(3-bromo-2,2-bis(bromomethyl)-1-propoxy)silane, $Si(OTBN)_4$, as would be expected for a compound in which the predominant grouping would be Si-OTBN. The ^1H NMR signals at 2.3 & 7.1ppm could be assigned to residual toluene. Three signals could be ascribed to Et_3NHCl as follows: δ: 1.38 (CH_3), 3.08 (CH_2) & 6.37 (NH). The integration of the CH_3:CH_2 signals supported this assignment. The CH_2 signal was not a simple quartet due to coupling with the NH proton. The major signals at 3.52 & 3.93ppm were both singlets, and there was no trace of a OH triplet, thus pointing to the absence of free alcohol. The signals were also shifted relative to those of the free alcohols, indicating reaction had occurred. The integration of these two major signals, at 2.7:1.0 (δ: 3.5:3.9) was close to that expected for the target species, assuming that the CH_2Br protons on the TBNO group resonated at a frequency very close to those on the ODBNO group, and similarly for the CH_2O protons. The integration would then be expected to be 48:16, or 2.5:1.0. The ^{13}C NMR shifts did not correspond to either TBNA or DBND, suggesting that some reaction had occurred, but were not conclusive. The white crytalline product was shown to be TBNA, either unreacted alcohol, or the product of the basic hydrolysis.

The white solid product in section 4.2.3 showed slight excess mass over that expected for the base hydrochloride, and this could be accounted for by some $Si(OTBN)_n$ species, as shown by the IR spectrum. The IR spectrum of the white resinous product in air showed absorption of water by the appearance of a large νOH band, but the rest of the spectrum remained unchanged, thus seeming to indicate that no large scale hydrolysis occurred, the OH band being merely due to water absorption or minor surface hydrolysis. The ^1H NMR spectrum was consistent with the presence of TBNO groups and linking ODBNO groups (δ: 3.44, 3.45, 3.84 & 3.86) together with small amounts of chelating ODBNO groups (δ: 3.61 & 4.07). This was supported by the ^{13}C spectrum which showed three types of CH_2O and CH_2Br groups, corresponding to the three types mentioned above. However, it was impossible to assign these signals with any certainty. The formation of the tacky gum in air could be due to atmospheric moisture hydrolysing the alkoxy groups and aiding ester interchange, thus producing $ODBNO^{linking}$ from $ODBNO^{chelating}$ and aiding polymerisation.

The excess mass of the LiCl (white solid) in section 4.2.4 could be accounted for by Si(ODBNO) species. The IR spectrum of the fawn resin product indicated the presence of SiOC bands, suggesting that reaction had occurred to produce some sort of silicon alkoxide, the material being hydrolytically unstable in air. The insolubility of the solid produced in NMR solvents made analysis difficult. However, the formation of a solid from the original resinous product could be due to polymerisation occurring between discrete silicon units containing $ODBNO^{chelating}$, which might be expected to be resinous, by opening up the ODBNO ring to produce linked systems, thus increasing the molecular weight of the product and thus its melting point. This area could benefit from further work.

The trisdioldiborate resin gave very clear ^{1}H & ^{13}C NMR spectra which enabled the chemical shifts to be assigned with confidence to the various atoms in the product on the basis of signal strength and the relative shift from the DBND resonance. Those signals due to the two cyclic ODBNO units are stronger and further removed from the DBND peaks than those of the linear, bridging ODBNO unit.

The initial solid white product in the $NaBH_4$/DBND reaction (section 4.2.6) was shown by its IR spectrum to be $NaBH_4$. The white precipitate finally produced did not show a simple ^1H NMR spectrum, although it did seem to indicate that the DBND had indeed reacted. The signals seen could not be assigned with any certainty. The insolubility of the material may have been due to linking of the boron units via ODBNO, though the four signals in the proton NMR could account for both linking and chelating units. This material has been produced before from DBND and boric acid, $B(OH)_3$, in methanol[22], but not by this route

4.4 References

1) Gustavson; J. Prakt. Chem., 1896, 54, 97.
2) Gustavson; J. Prakt. Chem., 1897, 56, 93.
3) N Zelinsky; Berichte, 1913, 46, 160-72.
4) H Bincer & K Hess; Berichte, 1928, 61, 537-42.
5) JC Krantz, C Jelleff Carr & SE Forman; J. Pharmacol., 1938, 64, 298-301.
6) W Kalow & S Schunk; Naunyn-Schmiedebergs Arch. Exptl. Pathol. Pharmacol., 1950, 211, 388-91.
7) RA Cass & LO Raether; ACS, Div. Org. Coatings, Plastics Chem., Preprints, 1963, 23(1), 82-94.
8) H Miyake, K Hayashi & S Okamura; J. Polym. Sci., A, 1965, 3(8), 2731-41.
9) WC Weaver & ER Larsen; ACS, Div. Org. Coatings, Plastics Chem., Paper, 1968, 28(1), 196-203.
10) DP Miller; Life Prop. Prot., Papers, Semi-annual Meeting, Fire Retard. Chem. Assoc., 1977, 130-55.
11) M Das, PJ Haines, TJ Lever & GA Skinner; J. Fire Retard. Chem., 1982, 9(1), 23-30.
12) e.g. JA Albright (Velsicol Chemical Corp.), GB 1517652. RHS Wang & JG Pacifici (Eastman Kodak Co.), US 4012466. AK Jung, J Siberberg & ED Weil (Stauffer Chemical Co.), US 4373103. Y Halpern (Borg-Warner Chemicals Inc.), US 4424172.
13) JW Lyons, "The Chemistry and Uses of Fire Retardants", Wiley-Interscience, New York, 1970, pp.14-17. EC Creitz, J. Res. Natl. Bur. Stand., 1970, 74A, 521. G Avondo, C Vorelle & R Delbourgo; Combust. Flame, 1978, 31, 7.
14) G Avondo, C Vouvelle & R Delbourgo; Actes Congr. Int. Composes Phosphores, 1st, 1977, 283-96.
15) SL Madorsky, "Thermal Degradation of Organic Polymers", Wiley-Interscience, New York, 1963. M Lewin & A Basch in M Lewin, SM Atlas & EM Pearce eds., "Flame Retardant Polymeric Materials", Vol. 2, Plenum Press, New York, 1978, pp.1-3.
16) PJ Haines, TJ Lever & GA Skinner; Thermochim. Acta, 1982, 59(3), 331-42.

17) RJ Harper (United States Dept. of Agriculture), US Pat. Appl. US 749905. MJ Keogh (Union Carbide Corp.), US 4444957.

18) CJ Del Valle & RA Hunter; Proc. Int. Conf. Fire. Saf., 1980, 5, 227-40. CJ Del Valle & RA Hunter; Proc. Annu. Conf. - Reinf. Plast./Compos. Inst., Soc. Plast. Ind., 1980, 35th (Rising Challenge 80's), 6-C, 1-6-C, 4.

19) G Saischek, K Wegleitner, F Heu & R Wolmuth (Chemie Linz A.-G.), Austrian 357336. G Saischek, K Wegleitner, F Heu & R Wolmuth (Chemie Linz A.-G., Lentia G.m.b.H. Chem. und Pharm. Erzeugnisse-Industriebedarf), Eur. Pat. Appl. 5497, Ger. Appl. 2820909.

20) H Mayerhoefer, W Mueller & U Sollberger (Sandoz Ltd.), Ger. Offen., 2238243.

21) HA Al-Madfa, RA Shaw & S Ture; P, S, Si, Relat. Elem., 1990, 53(1-4), 333-8.

22) G Siaechek, K Wegleitner, F Heu & R Wohlmuth; Eur. Pat. Appl. 5,497 (Ger. Appl. 2,820,909).

CHAPTER FIVE

5 Thermal Testing

5.1 Introduction

There are many methods which are used to test potential flame retardants. Some are as simple as melting point determination, as substances which melt at too low a temperature would have a high tendency to melt and leach out of the polymer before the temperature was high enough to cause the polymer to burn, thus proving ineffective as additive flame retardants when ignition finally occurred and through the subsequent fire. Other tests are more specialised, involving samples of polymer or fabric substrate impregnated with the potential flame retardant, and require that the sample be prepared much as it would be produced on a large scale, e.g. by dip-coating a fabric or melt processing a polymer. These tests are often used as standards by organisations such as ASTM (the American Society for the Testing of Materials) and are adopted by fire legislation, which is becoming ever more stringent.

Perhaps the most common preliminary methods, however, of testing the potential flame retardants themselves are the various thermal analysis techniques available. The most common of these are differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The former produces a plot of energy input vs. time and heats a sample at a constant rate, thus showing endothermic and exothermic changes to the sample and enabling heat input and output to be calculated. The latter is simply a measure of the weight of the sample with temperature at a constant heating rate, and can be very useful in attempting to identify the various species evolved and the residue remaining. Such techniques are useful in determining the ability of the potential flame retardant material to absorb thermal energy, which could otherwise be use to heat the substrate to its ignition point or sustain combustion. They can also show any large exotherms which would be undesirable for a flame retardant. Lastly, they are very useful for pinpointing the decomposition temperature of a species and also at what temperature the weight loss occurs during decomposition. This is especially important for flame retardants which act in the gas phase, as the species detailed in this work do to the greater extent.

Generally, the points arising from such thermal analysis which would be desirable in a flame retardant are:

* Reasonably high melting point. As suggested above, too low a melting point would allow the flame retardant to leach away from points of heating, thus losing effectiveness.

* Reasonably high decomposition temperature. This ideally needs to be in the same temperature range as the decomposition temperature of the substrate, or slightly lower. Thus, as the substrate degrades, any gas-phase active flame retardant species are being formed at the same time and can show maximum effectiveness.

* A TGA profile which matches that of the substrate as closely as possible. Thus, if the substrate decomposes quickly, losing its weight rapidly as volatile degradation products, the flame retardant also needs to decompose quickly, producing the flame retardant species needed to combat the fast rise in combustibles. Conversely, if the substrate decomposes slowly, so must the flame retardant to ensure that there are active species present during the whole decomposition period of the substrate.

However, there are no hard and fast rules for determining from these types of tests what species will be good flame retardants in practice. Further tests would be needed to determine that, involving samples produced using the actual methods that would be used in the final product, e.g. to ensure that the materials are compatible, and that the flame retardant species does not decompose during polymer processing. Even then, controlled tests would still not be exact parallels of what would happen in a real fire.

Three test systems were used on the materials produced in this study:

1) DSC from room temperature to 400°C with a paper trace.
2) DSC from room temperature to 400°C with computer datalogging.
3) DSC & TGA to higher temperatures (up to 900°C) on certain samples.

The first of these methods gave a visual indication of the thermal behaviour of the samples up to 400°C, any exotherms or endotherms being measured using the second method. The higher temperature analyses were run at Octel in Ellesmere Port.

5.2 DSC and TGA Results

5.2.1 Tris(3-bromo-2,2-bis(bromomethyl)-1-propoxy)phosphate (III)

An endotherm at 88°C (25J/g, 25kJ/mol) corresponded to fusion of the sample. A broad exotherm then appeared at 202°C (92J/g, 92kJ/mol), followed by a larger, sharper signal at 291°C representing a large exotherm of 318J/g, 319kJ/mol (see page A-23).

5.2.2 Tris(3-bromo-2,2-bis(bromomethyl)-1-propoxy)phosphate (V)

An endotherm at 165°C represented the melting of the sample, with a heat of fusion of 30J/g, 30kJ/mol. There was another broad exotherm around 360°C (150J/g, 152kJ/mol), followed immediately by an exotherm around 370-80°C (169J/g, 173kJ/mol) (see page A-24).

5.2.3 Tris(3-bromo-2,2-bis(bromomethyl)-1-propoxy)borane

To 400°C this species showed only an endotherm at 132°C of 49J/g, 48kJ/mol, due to the melting of the compound, indicating that no large scale decomposition of the sample occurred in this temperature range. A more detailed analysis revealed that an endotherm at ~400°C coincided with the maximum rate of weight loss, all volatile components having been evolved by ~440°C. This represents the decomposition of the material, the 5.1% w/w residue corresponding to B_2O_3 (see pages A-25 & A-26).

5.2.4 Tris(3-bromo-2,2-bis(bromomethyl)-1-propoxy)boroxine

This material again showed only an endotherm at 145°C (63J/g, 66kJ/mol) due to the melting of the sample. Otherwise, the sample appeared to be stable to 400°C.

5.2.5 N-triphenyl-B-tris(3-bromo-2,2-bis(bromomethyl)-1-propoxy)borazine

An endotherm at 165°C (38J/g, 49kJ/mol) corresponded to the sample melting, with a slight endotherm at 137°C possibly due to loss of toluene from the sample, as this species showed evidence of having crystallised as the toluene solvate. At 340°C a large exotherm (736J/g, 949kJ/mol) occurred (see page A-27).

5.2.6 N-tris(4-bromophenyl)-B-tris(3-bromo-2,2-bis(bromomethyl)-1-propoxy)borazine

A broad endotherm peaking at 180°C (23J/g, 34kJ/mol) corresponded to the melting of the sample. The long attack to this signal, from ~150°C, may be due to the loss of toluene, as this sample also appeared to crystallise as the toluene solvate. From ~275°C to 400°C there was a pattern of exotherms, together representing 661J/g (see page A-28).

5.2.7 Tris(3-bromo-2,2-bis(bromomethyl)-1-propoxy)aluminium (III)

This sample showed several signals. Three endotherms appeared, at 75°C, 148°C & 186°C, the last two together representing 21J/g. There was also a sharp exotherm at 289°C (12J/g) followed by a general broad exotherm to 400°C (see page A-29).

5.2.8 Tetrakis(3-bromo-2,2-bis(bromomethyl)-1-propoxy)silane

This sample showed an endotherm at 102°C (37J/g, 49kJ/mol) due to fusion, and an endotherm from ~390-400°C. On a higher temperature run, this endotherm was seen to peak at ~400°C, corresponding to the maximum rate of weight loss. The TGA trace showed that by ~450°C, 95% of the mass had been lost, the residue corresponding to SiO_2 (see pages A-30 & A-31).

5.2.9 Bis(3-bromo-2,2-bis(bromomethyl)-1-propoxy)zinc (II)

This showed a complex trace with exotherms at 37 & 90°C, and an endotherm at ~120°C due to melting (6J/g, 4kJ/mol). The small apparent size of this endotherm was probably due to some overlap with the exothermic signal at 90°C. This was followed by a large exotherm at 187°C (257J/g, 183kJ/mol). No further signals were seen to 400°C (see page A-32).

5.2.10 Tetrakis(3-bromo-2,2-bis(bromomethyl)-1-propoxy)titanium (IV)

An endotherm at 90°C represented melting, and was accompanied by a smaller endotherm at ~70°C, their proximity making the measurement of the enthalpy of fusion difficult, but together the signals represented 32J/g, 43kJ/mol. The signal was then stable until another endotherm at 327°C (28J/g, 38kJ/mol), followed by a broad exotherm to 400°C (see page A-33).

5.2.11 Bis(3-bromo-2,2-bis(bromomethyl)-1-propoxy)magnesium (II)

Melting occurred at 165°C with a sharp endotherm (54J/g, 36kJ/mol). Broad signals appeared at 275°C (endotherm, 29J/g, 20kJ/mol) and immediately following (exotherm to 400°C) (see page A-34).

5.2.12 Sodium bis(2,2-bis(bromomethyl)-1,3-propandioxy)borate

This species showed three small endotherms to 200°C: 88°C (22J/g, 12kJ/mol), 109°C (15J/g, 8kJ/mol) & 195°C (2J/g, 1kJ/mol). Two exotherms followed: 202°C (2J/g, 1kJ/mol), 299°C (34J/g, 19kJ/mol), with a general exotherm to 400°C.

5.2.13 (3-bromo-2,2-bis(bromomethyl)-1-propoxy)lithium

This showed a complex thermal behaviour, with four major endotherms before 300°C, at 85°C, 160°C, 200°C & 230°C. After the first two events, the mass had dropped to 78% of the initial mass, dropping during the second two endotherms to 28%, possibly representing LiBr. Two further endotherms occurred at 480°C and 530°C, together with a broad endothermic signal peaking at ~830°C which corresponds to the loss of the remaining mass, possibly due to volatilisation of the LiBr (see page A-35).

5.2.14 3-bromo-2,2-bis(bromomethyl)-1-propanol (TBNA)

This showed an endotherm of 87J/g, 28kJ/mol, due to fusion, and a large exotherm at ~250°C (378J/g, 123kJ/mol).

5.2.15 2,2-bis(bromomethyl)-1,3-propandiol (DBND)

The enthalpy of fusion of this compound was measured as 124J/g, 32kJ/mol. Another endotherm occurred at 303°C (69J/g, 18kJ/mol), and a broad exotherm to ~380°C.

5.3 Weight Loss Results

Sample	Weight loss (% w/w)
$P(OTBN)_3$	79
$P(O)(OTBN)_3$	92
$B(OTBN)_3$	56
$(TBNOBO)_3$	55
$(C_6H_5NBOTBN)_3$	49
$(4\text{-}BrC_6H_4NBOTBN)_3$	48
$Al(OTBN)_3$	97
$Si(OTBN)_4$	67
$Zn(OTBN)_2$	59
$Ti(OTBN)_4$	90
$Mg(OTBN)_2$	77
$NaB(ODBNO)_2$	75
Li(OTBN)	59
TBNA	91
DBND	98

Table 5-I: Weight loss to 400°C

5.4 Discussion and Conclusions

Many of the samples tested showed large exothermic signals below 400°C. Such behaviour could be detrimental to the performance of these species as flame retardants, as they would be *adding* heat to the system and not absorbing and dissipating it. The two borazines showed particularly large exotherms over a broad temperature range. The phosphate (III) showed two large exotherms below 300°C and the zinc species one below 200°C. The phosphate (V) also showed an exotherm just below 400°C.

The ortho and metaborates, together with the silicate species showed only endotherms, due to melting and decomposition. As the silicon species appeared to fulfil the initial criteria, available from these tests, of a potential flame retardant, further TGA work on them, together with the metaborate, may be worthwhile.

The weight loss profiles of the orthoborate and silicate species were compared with an acrylonitrile-butadiene-styrene polymer and a flame retardant species being developed at Octel. Generally, for good flame retardant effect, the TGA profile should match that of the polymer substrate reasonably closely. This is in order that the active flame retardant species are around at the same time as the flammable volatiles produced by polymer degradation.

The TGA profile of $B(OTBN)_3$ showed that it decomposed and lost weight over quite a broad range of temperature, from ~150-400°C, most weight loss occurring before ~350°C. The polymer did not begin to degrade until ~350°C, indicating that the $B(OTBN)_3$ would probably have emitted the bulk of the active HBr species *before* the polymer started to burn. A sample of $B(OTBN)_3$ held at 250°C for an hour lost 50% of its weight.

The $Si(OTBN)_4$ profile, on the other hand, was much narrower, decomposition starting at ~300°C and continuing to 400°C. In fact, the profile was very close to that of the flame retardant under development.

Both species decomposed a few degrees before the polymer, indicating that the active flame retardant species *would* be present during polymer combustion, and could thus be effective in retarding the spread of fire.

It is difficult to draw any conclusions from the weight losses of the samples up to 400°C. Values close to 100% indicate that all the active species have been evolved before the ABS polymer would start to burn. $Si(OTBN)_4$ lost only 67% of its mass, so samples showing similar weight losses may also be worth testing. However, other factors must be taken into account, e.g. $B(OTBN)_3$ lost 56%, but over a broad range of temperature, whereas $Zn(OTBN)_2$ lost 59%, but has a large exotherm at 187°C.

Thus it can be seen that whereas DSC is a useful technique for initial screening of potential flame retardant materials, further tests need to be performed in order to explore further the suitability of a particular compound.

CHAPTER SIX

6 Some Reactions of Alkali Metal Tetrahydridoborates with 1,2-Dihydroxybenzene and Sulphur

6.1 Introduction

As has been mentioned earlier, species containing two hydroxyl groups can undergo elimination reactions with reactive compounds such as halides or acids to give a variety of products:

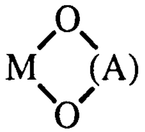
(1) Hydroxy alkoxides.

$$MX + HO\text{-}(A)\text{-}OH \longrightarrow M\text{-}O\text{-}(A)\text{-}OH + HX$$

(2) Linked, concatenated systems.

$$2\,MX + HO\text{-}(A)\text{-}OH \longrightarrow M\text{-}O\text{-}(A)\text{-}O\text{-}M + 2\,HX$$

(3) Chelated systems.

MX_2 + HO-(A)-OH $\longrightarrow$  + 2 HX

Where (A) is a divalent organic group, e.g. $(CH_2)_n$, M is a metal or metalloid, and X is a reactive group, e.g. a halogen.

The particular reaction pathway which prevails depends on several factors:

- The effect of the bound M on the reactivity of the remaining hydroxyl.
- The dilution and ratio of the reactants.
- The size of the ring that would be formed by chelation.

If the bound M made the remaining hydroxyl less reactive, the product of reaction (1) may predominate. If it made it more reactive, but the diol were present in lesser concentration than the reactive MX species, the product of reaction (2) may be the most common. If the hydroxyl were made more reactive and there were more diol than MX_n present, chelation may be favoured, depending on the size of the ring that would be formed. This latter option, reaction (3), would be most favoured if the hydroxyls were separated by two or three carbon atoms, thus forming five or six membered rings respectively on chelation. These have been observed in the case of M = boron, when cyclic esters of boric acid are formed from the reaction of $B(OH)_3$ and diols[1], or by the reaction of other reactive boron compounds with diols.

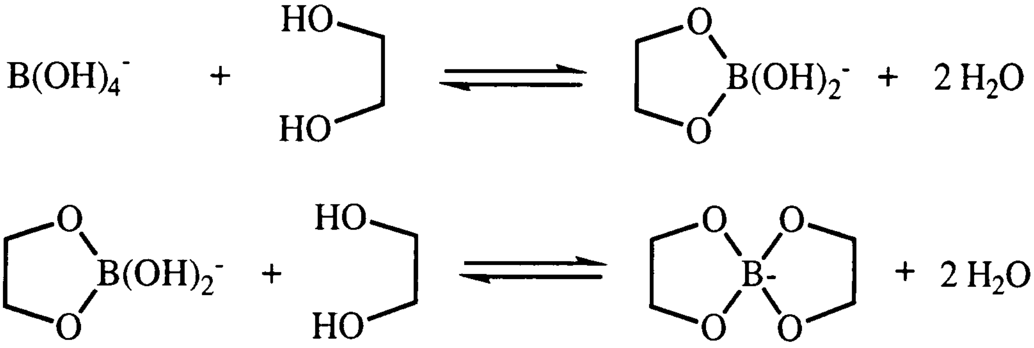
These reactions were first studied in detail by Boeseken *et al* in 1918[2], as it had been noticed in the latter years of the nineteenth century that the addition of diols to aqueous solutions of boric acid resulted in changes to some of the physical properties of the solution, such as acidity, conductivity, and their rotation of the plane of polarised light, this latter point being especially interesting. Boeseken found that the reaction of potassium borate and catechol (1,2-dihydroxybenzene) in water resulted in the formation of a complex which precipitated from the concentrated aqueous solution. He also managed to isolate the rubidium and ammonium salts, and suggested that these crystals were free of water of crystallisation. Various anilinium salts, on the other hand, were found to contain water of crystallisation, on the basis of elemental analysis. However, the formulae they proposed, based on the same analyses, suggested ratios of catechol to boron in the salts of from 2:3 to 3:2, though they did have some difficulty in analysing for boron. They did not suggest any definite structures for these complexes. In 1925, Hermans and Meulenhoff, in the same issue of a journal (Z. Anorg. Chem.), published papers on this topic. Hermans' paper dealt with a range of organoboron complexes prepared from boric acid and a range of diol-type species, including hydroxy carboxylic acids such as salicylic acid (2-hydroxy benzoic acid), as well as simple 1,2-diols, such as pentan-2,4-diol[3]. He proposed structures containing a tetracoordinate boron atom coordinated by the four oxygen atoms of two of the diols. These he regarded as derivatives of the simple borate anion, $B(OH)_4^-$, and he also suggested the formation of the intermediate products, containing only one coordinating diol per boron atom. Meulenhoff, in his paper, prepared similar compounds, but took particular notice of those formed from unsymmetrical diol-type species, such as salicylic acid or mono-substituted catechols, as these were optically active[4]. This behaviour Meulenhoff explained by suggesting that the central boron atom was tetrahedrally coordinated (the anionic boron species being isoelectronic with carbon), and thus forming "spiroborate" complexes. He also claimed to have prepared the free acid of the biscatecholato borate by subliming the anilinium salt *in vacuo*.

The salts isolated often gave poor crystals, unsuitable for X-ray analysis, due to the variable number of molecules of water associated with the borate anion in the crystals. Even the potassium salt, which Boeseken had claimed was free of water, resisted X-ray analysis. The structure of the salts in solution was apparent from their optical properties, which showed that some form of tetrahedral boron centre must be present. However, in solution a complex series of equilibria is set up between the boric acid (or other boron source, e.g. borax or metaboric acid, as in alkaline solution the anions of these species are related by a series of equilibria[5]), and the diol. The position is further complicated when the diol used is acidic, e.g. in the case of catechol, which has an acidity similar to that of boric acid.

In solution in water, $B(OH)_3$ acts as a weak, monobasic Lewis acid, accepting OH^- to form the borate anion, $B(OH)_4^-$. Thus:

$$B(OH)_3 + 2\,H_2O \rightleftharpoons B(OH)_4^- + H_3O^+$$

This borate ion can then interact with the diol to give the monodiol and bisdiol complexes:



The boron-diol complexes are favoured by alkaline conditions, and, depending on the diol used, the intermediate monodiol dihydroxy borate complex can sometimes be isolated as a salt as well as the bisdiol complex. The bisdiol salts appear to be more likely to crystallise if they are of high symmetry, e.g. biscatechol or bispinacol[5].

Studies on these two sets of complexes gave indications as to their structure. The monodiol complexes were studied by Dale, who used elemental analysis and thermal dehydration curves to determine their structure[5]. The bisdiol complexes had, of course, been studied by Hermans[3] and others[2,4,6].

The most common boron sources used in aqueous solution are:

- * orthoboric acid, $B(OH)_3$
- * metaboric acid, $(HOBO)_3$
- * borax, $Na_2B_4O_7.10H_2O$

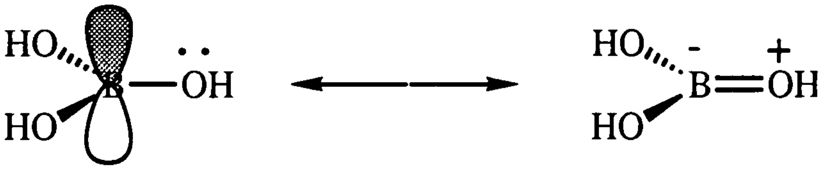
When dissolved in water, these various species are readily interconvertible, especially in the presence of base, OH^-. Orthoboric acid itself is a weak, monobasic acid which acts exclusively as an electron pair acceptor, i.e. a Lewis acid, and in solution in water can coordinate with H_2O to release a proton and form the simple borate anion:

$$B(OH)_3 + 2\,H_2O \rightleftharpoons B(OH)_4^- + H_3O^+$$

This equilibrium represents the two most important coordination environments for B-O compounds:

- * three coordinate neutral trigonal planar
- * four coordinate anionic tetrahedral

The weakness of boric acid in this situation is accounted for by the fact that in the trigonal planar configuration there is mesomeric stabilisation between the boron and the O:



This sort of stabilisation is not possible in the tetrahedral structure, hence the larger B-O distance in the borate anion (1.48Å vs. 1.37Å in $B(OH)_3$).

Metaboric acid is, in effect, a dehydrated form of orthoboric acid, and can be formed by heating the orthoboric acid to drive off water. It has a six-membered ring structure with alternating boron & oxygen atoms, with each boron also having an attached hydroxyl group:

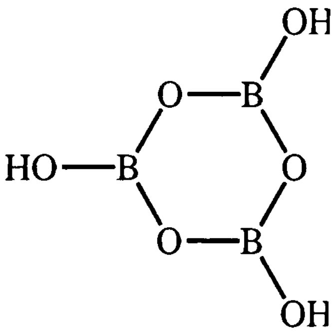


Fig. 6-I: The structure of metaboric acid.

This ring structure is very stable due to the same mesomeric effects between boron and oxygen observed in orthoboric acid. Here, however, it is extended over a ring system, which can be regarded as being quasi-aromatic. This system is, of course, isoelectronic with 1,3,5-trihydroxy benzene. In solution, this system can also accept base, OH^-, to yield a system containing two trigonal and one tetrahedral boron. Such a system can also be formed from the condensation of two $B(OH)_3$ and one $B(OH)_4^-$.

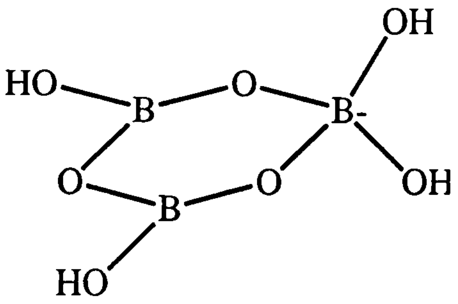


Fig. 6-II: The structure of the monohydroxy metaborate anion.

The single tetrahedral boron can be accommodated in the planar ring structure, although some stabilisation is lost. Further reaction of one of the other trigonal boron atoms with OH^- forces the ring to bend to accommodate the bond angles, thus losing further stabilisation. This also introduces an axial interaction between the OH groups on the tetrahedral boron atoms, which causes yet further destabilisation. OH^- attack on the remaining trigonal boron atom would introduce two further such axial interactions, which would be highly unfavourable and is not observed. Instead, the two axial hydroxyl groups can condense with $B(OH)_3$ to form the $B_4O_5(OH)_4{}^{2-}$ ion, which is the structure in solution of the borax anion:

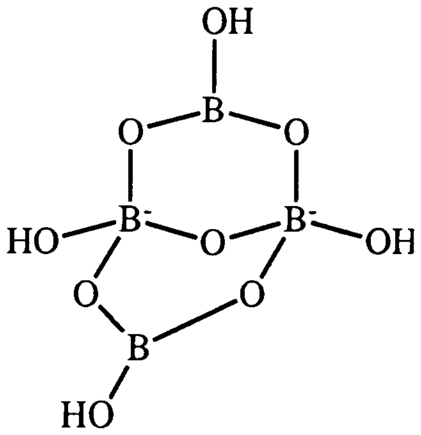


Fig. 6-III: The structure of the $B_4O_5(OH)_4{}^{2-}$ anion.

This species now contains two trigonal boron atoms, and if they were each to react with OH^-, the steric situation resulting would clearly be impossible. However, if such a reaction took place with elimination of H_2O, the system could form a cage structure of fused, six-membered B_3O_3 rings, similar in structure to the organic compound adamantane:

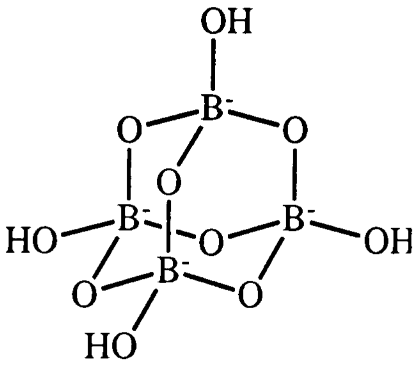
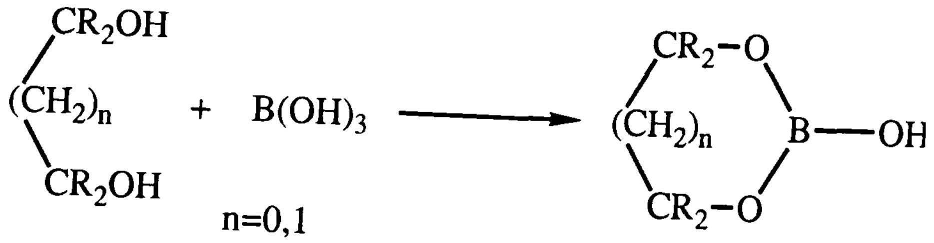


Fig. 6-IV: The structure of the borate(4-) anion cage.

In dilute solutions of boric acid, the simple, monomeric trigonal and tetrahedral structures exist, but as the concentration increases, the boron units begin to link up in a complex series of equilibria into oligomeric and polymeric borate anions, such as those outlined above. Thus it can be seen how in aqueous solution, ready interchange is possible between the various types of borate anion.

It has been mentioned before that boron sources such as $B(OH)_3$ can react directly with alcohols to form boric acid esters. These are generally prepared by removing the water as an azeotrope in a non-aqueous system, as they tend to hydrolyse fairly readily. If diols are used instead of monohydroxy species, it is possible to form cyclic esters where the diol is chelating the boron atom. In his 1925 study, Hermans looked at the reactions of $B(OH)_3$ with a range of 1,2 and 1,3-diols[3].

He found that the cyclic esters of 1,3-diols were more readily formed than those of 1,2-diols:



This is in marked contrast to the case of the mono and bisdiol complexes formed in aqueous solution, where the 1,2-diols are favoured over the 1,3-diols[5]. Initially it was thought that this was due to the difference in the O-O distance for the trigonal boron (2.32Å) being less than that of the tetrahedral boron (2.42Å)[7]. However, later measurements showed that the difference in the O-O distance was much less marked than this, and unlikely to cause the stability difference observed[8].

In 1961, Dale and others performed a series of studies involving boric acid esters and complexes with a range of 1,2 and 1,3-diols[1,5,9]. They proposed that, whereas both diols can form cyclic monodiol esters, in the case of 1,3-diols, the 120° OBO angle necessary for maximum stabilisation of the trigonal BO_3 unit can easily be accommodated in the resultant six-membered ring. The planar five-membered ring formed by 1,2-diols, on the other hand, is very strained as it requires a 108° OBO bond angle, so the trigonal boron in this case is destabilised. It can, however, be stabilised by base attack, the incoming base donating an electron pair to the trigonal boron to form a tetrahedral B^- centre, the resulting bond angle of some 109° being easily accommodated in the five-membered ring. So it can be seen that in aqueous solution 1,2-diols will preferentially form tetrahedral borate complexes, as these remove the strain in the rings formed. The monodiol dihydroxy complexes can be formed by water attack on the trigonal boron, thus increasing the acidity of the solution, and in some cases the bisdiol borate can be isolated from solution. Also, studies of the reactions of 1,2-diol boric acid esters with N bases such as benzylamine and pyrrolidine showed that there was a large exotherm on mixing which was not observed with similar 1,3-diol esters[1]. Although the complexes formed could not be isolated, this work nonetheless indicated that the strain caused by a trigonal boron atom in a five-membered ring was being relieved by ready reaction with a Lewis base.

1,3-diols, on the other hand, do not generally increase the acidity of boric acid solutions. In this case, both the trigonal 120° or tetrahedral 109° angle can be accommodated within a six-membered ring, so there is no strong driving force for the boron to forsake its mesomeric stabilisation by base attack to form the tetrahedral B^- centre. In the case of substituted 1,3-diols, the formation of a complex can be sterically disfavoured, if not completely precluded. The reasons for this are the unfavourable axial interactions between groups on the diol and the axial OH on boron:

Fig. 6-V: Unfavourable axial interactions in borate anions.

These types of interaction can, of course, also destabilise the ester, but to a lesser extent, e.g. 2,4-dimethyl-2,4-pentandiol *will* form an ester, but *not* a complex (one axial interaction in the ester vs. three in the dihydroxy complex). Distillation of cyclic 1,3-diol esters is possible to yield the unchanged compound, whereas the cyclic 1,2-diol esters generally condense in the form of extended polymers (reaction type (2), above)[1].

The structure of the diols themselves is also important. Ethylene glycol does not form complexes in aqueous solution (it does not raise the conductivity of boric acid solutions above the level due to the free glycol[6]) because, as there is free rotation about the C-C bond, the hydroxyl groups tend to position themselves 180° apart due to their mutual repulsion. At the other extreme, e.g. *cis*-cyclopentan-1,2-diol or catechol, it is seen that complexes are formed very readily, as the two hydroxyl groups are held in the same OCCO plane and are thus readily able to react with the $B(OH)_3$. *Trans*-cyclopentan-1,2-diol does *not* form complexes, as the hydroxyl groups are held apart in an unfavourable configuration.

Aromatic 1,2-diols and five-membered alicyclic *cis*-1,2-diols in general will readily form complexes, whereas the *trans*-1,2-diols will not. The situation with six-membered 1,2-diols is more complicated. In this case, there is no difference between the *cis* and *trans* forms, as in the *cis* isomer, the hydroxyls are always 60° apart, and in the *trans* form they interchange between 60° in the diequatorial and 180° in the diaxial configurations. They thus show the same effect on the conductivity of boric acid solutions, which is much smaller than that observed for 1,2-diols. Boeseken[6] used this observation as proof of Sachse's 1890's theory[10], refined by Mohr in 1918[11], that the cyclohexane ring is non-planar, as if it were not, there would be a large difference in the effect of the *cis* and *trans* configurational isomers on the conductivity of $B(OH)_3$ solutions.

Boeseken used these differences in a series of studies of carbohydrates. These were, and are, extremely important compounds in such forms as cellulose, sugars, and, as we now know, the backbone of the DNA polymer on which life on this planet is based. Indeed, some of the earliest chemical experiments were probably performed on a simple carbohydrate such as sucrose, or its component glucose. It was early found that the action of some yeasts on these materials produced dilute solutions of ethanol. Their structure had been studied extensively in the nineteenth century by such chemists as Baeyer, Berthelot, Dumas, Fittig and Tollens, and Emil Fischer received the Nobel Prize in 1902 for his elegant work in this area. Boeseken, in the early years of the twentieth century, studied the effects of various carbohydrates on the conductivity of boric acid solutions[6,12]. He was able to show the relationships in solution between the furanose and pyranose forms of various common carbohydrates, and their interchange via a hydrate intermediate, and was also able to assign configurations to their various forms.

Another use to which these properties can be put is in the separation of isomers of diols in cases where the isomers react to give different products with boric acid and borates. For example, *trans*-cyclohexane-1,3-diol forms a polymer with borates, whereas the *cis* isomer forms a cyclic ester which can be removed from the mixture by distillation. The diols can then be regenerated by alkaline hydrolysis of the ester and polymer.

Yet another use for borate complexes is in Boron Neutron Capture Therapy (BNCT) of cancer tumours. In this method of treatment, a molecule containing ^{10}B is injected into the body where it selectively binds to the tumour cells. The affected area is then irradiated with thermal (low energy) neutrons. ^{10}B has a large cross section to such neutrons, i.e. there is a large probability that a passing neutron will interact with the nucleus of the boron atom; in effect, it presents a large cross sectional area to neutrons. If reaction occurs, an atom of ^{7}Li and an α particle are formed:

$$^{10}_{5}B + ^{1}_{0}n \longrightarrow ^{7}_{3}Li + ^{4}_{2}\alpha$$

The α particle then carries the kinetic energy of the neutron away from the reaction site. Normally, α emitters are a low radiation hazard to humans, as the α particles they emit are easily absorbed in the top layer of skin, which normally consists of dead cells. Within the body, however, they can cause damage to living tissue, and, when present in sufficient concentration at a tumour cell, can kill it. This simple outline hides many problems, not least of which is the question of how to concentrate a boron-containing compound at a tumour site. Boron does not occur naturally in living cells, so there is no boron-containing natural product molecule to use as a starting point in the search for a suitable species. However, there are natural products which contain in their structure a diol grouping which could be used in combination with boron in the ways outlined above.

One such species is L-dopamine:

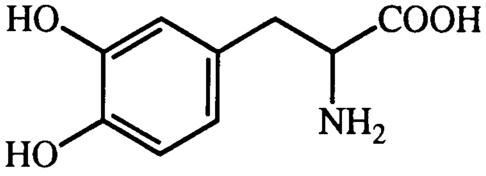
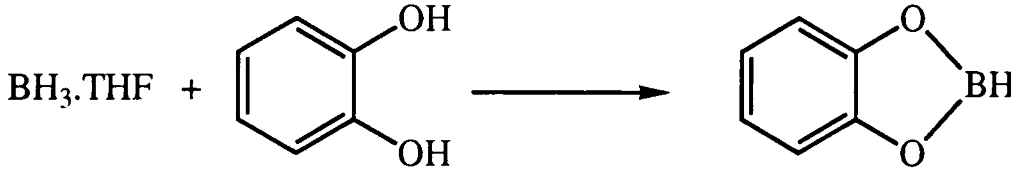


Fig. 6-VI: The structure of L-dopamine.

L-dopamine is a precursor of melanine, which in turn is produced in malignant melanoma tumours. The aromatic 1,2-diol grouping is not directly involved in the action of the molecule, so this offers a method of attaching boron to the molecule. In aqueous solution, borax and L-dopamine form the type of anionic borate complex outlined above, and such complexes can be injected into the body to attach the boron to the tumour[13]. However, the concentration of boron thus provided would not be nearly enough to achieve a reasonable effect on the tumour, as each carrier would only contain one boron atom. Many more than this, perhaps even hundreds of ^{10}B atoms, would need to be brought to a tumour cell for effective treatment, as, although ^{10}B does have a large thermal neutron cross section, the interaction between neutrons and matter is still not very strong (when compared to charged particles and electromagnetic radiation). One way of achieving such a concentration may be to attach pendant carborane groups through their carbon atoms, which would be stable under *in vivo* conditions, and would provide large numbers of boron atoms in compact units. Such drugs would be used in conjunction with high intensity neutron sources such as that at Grenoble in France.

Other boron sources than boric acid and borates can also be used to prepare esters and borate complexes. BCl_3 with alcohols offers a route to esters, including cyclic esters, as does borane, BH_3.

The reaction of catechol with BH_3 in the form of BH_3.THF at 0°C yields catecholborane (1,3,2-benzodioxaborole) in which the boron is bound to the two oxygen atoms of a chelating catecholato group and one residual hydride:



Hydroboration of alkenes and alkynes had been pioneered as a synthetic method in organic chemistry by Brown *et al.* in the early 1960's[14]. Indeed, the sheer volume of papers on the subject by Brown and coworkers is a tribute to his contribution to this field, in which he has spent most of his career. Hydroboration yields alkyl or alkenyl boranes in a stereoselective reaction in which the boron preferentially binds to the less substituted carbon of the alkene/alkyne, by cis addition to the less hindered face of the double bond in the case of alkenes. It is tolerant of a range of substituents on the alkene/alkyne, provided that they are not readily reduced by B-H. The principle use of the reaction, however, involves the further reaction of the alkyl/alkenyl boranes with a variety of reagents to yield a range of products, e.g. oxidation with alkaline H_2O_2 to yield the alcohol (in effect, anti-Markownikoff addition of H_2O to the double bond of an alkene) or a carbonyl compound (from an alkyne); protonolysis with organic acids to yield the alkane/alkene. Because of the stereoselective nature of the hydroboration step, the subsequent steps yield products of known stereochemistry, e.g. 1-methylcyclohexene yields the *trans*-2-methylcyclohexan-1-ol on hydroboration and alkaline oxidation.

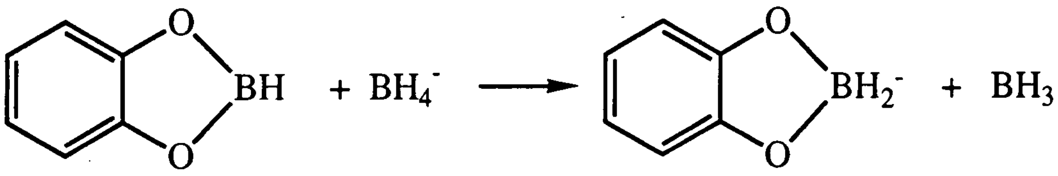
A variety of borane reagents is available for this reaction, ranging from diborane itself, B_2H_6, to mono & dialkylboranes and mixed dialkylboranes. These latter compounds, having a greater steric requirement than BH_3, are less reactive and more selective than borane itself and offer greater directional control of the reaction.

Catecholborane was first prepared in 1968 and quickly became recognised as a useful hydroborating agent. It shows greater selectivity than BH_3, is fairly stable to heat and atmospheric moisture, and has the advantage that the catechol group can be removed by reduction with, e.g. AlH_3, to yield the monoalkylborane, or by hydrolysis with water to yield the alkyl/alkenylboronic acid. Reaction with alcohols gives the boronic acid esters. It can also be used as a reducing agent, having properties complementary to those of other borane reagents. For example, it can perform reductions selectively in the presence of many alkenes[15].

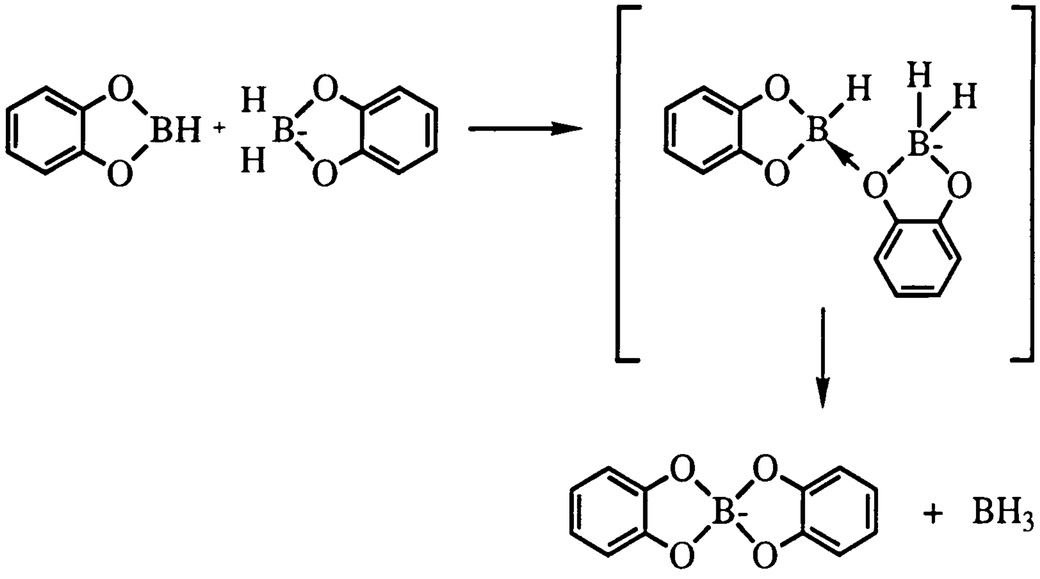
Sodium borohydride is also a very useful reagent in organic synthesis. It is used extensively as a nucleophilic hydride transfer reagent in the reduction of, e.g. carbonyls to alcohols, its utility lying in the fact that it does not readily attack C=C double bonds. Similarly to the borane reagents outlined above, modified borohydride reagents are available which have slightly different properties from the parent, BH_4^-. A range of trialkylborohydride reagents is marketed which are more nucleophilic than BH_4^- due to the inductive effect of the alkyl groups, e.g. "Super Hydride", $LiBHEt_3$; "L-Selectride", $LiBH^{sec}Bu_3$.

Electron withdrawing groups on boron, on the other hand, make the reagent less nucleophilic, less reactive and more selective. For example, $NaBH_3CN$, which can be used in acid solution, and $NaBH(OAc)_3$, which can be used selectively to reduce aldehydes in the presence of ketones. Borohydride reagents containing alkoxy groups are comparatively little known, and it was thought to be of interest to prepare such systems to study their properties.

The attachment of a chelating catecholato group onto borohydride would provide a dihydrido species with an electron withdrawing group, thus hopefully making the species formed less reactive and more selective. Such a species had been postulated by Männig & Nöth[16] in 1985 in a study of the reactions of $NaBH_4$ with catecholborane and the triscatechol diborate ester. They proposed that the dihydrido species, formed from the reaction of BH_4^- with catecholborane:



would be destroyed by Lewis acid attack of catecholborane on an oxygen atom of the dihydrido species, as shown over the page.



They did not, however, try the system $NaBH_4$/catechol, in which there would be no Lewis acid present. It was thought that this system may possibly produce the monocatecholatodihydrido species by reaction of one equivalent of catechol with one equivalent of BH_4^-, the chelating catecholato group making the remaining hydride hydrogen atoms less reactive and thus stopping the reaction at this stage. Isolation of a solid product was an early objective, but studies on solutions of such species would also prove to be of interest.

The reactions between alkali metal borohydrides and elemental sulphur have been studied previously in both the solid state[18,19,20] and, to a lesser extent, in various solvent media[17,20]. In the solid state, the dry, powdered species were mixed in the relevant proportions and heated to temperatures between 160 & 300°C. This type of treatment gave predominantly alkali metal thioborates and a gas, either hydrogen (H_2) or hydrogen sulphide (H_2S). A summary of the reactions reported is given over the page.

$$LiBH_4 + 4\,S \longrightarrow LiBS_2 + 2\,H_2S$$

$$LiBH_4 + 2\,S \longrightarrow LiBS_2 + 2\,H_2$$

$$LiBH_4 + 3\,S \longrightarrow LiB_3S_2H_6 + H_2S + 3\,H_2$$

$$LiBH_4 + S \longrightarrow LiBH_3(SH)$$

$$MBH_4 + 4\,S \longrightarrow MBS_2 + 2\,H_2S \quad (M = Na, K, Li)$$

$$MBH_4 + 3\,S \longrightarrow MBS_3 + 2\,H_2 \quad (M = Na, K)$$

$$NaBH_4 + 3\,S \longrightarrow NaBH_2S_3 + H_2$$

(Refs. 17-20.)

The presence of solvent seemed to complicate the reactions, and a variety of products was reported, depending on the solvent used, the temperature of the reaction, the reactant ratio and the particular alkali metal used. However, all such reactions at room temperature involved the evolution of H_2.

Lalancette *et al.* studied the reaction of the alkali metal borohydrides, mainly $NaBH_4$, with elemental sulphur in 1967[20], and reported the formation of a new species, "$NaBH_2S_3$", with the evolution of H_2 (the last reaction above). This conclusion was based on gas evolution data which indicated that the amount of H_2 evolved increased linearly with the ratio of sulphur to $LiBH_4$ up until a ratio of 3:1, after which no further H_2 was evolved. Also, elemental analysis for Na and B appeared to support this conclusion. However, this product was never isolated in crystalline form for X-ray analysis, though structures were proposed for both the monomeric and dimeric forms of the anion.

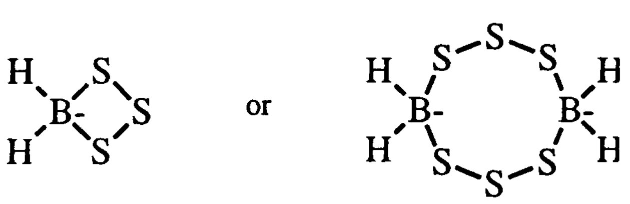


Fig. 6-VII: The proposed structures of the "$BH_2S_3^-$" anion.

The group went on to study the reducing properties of solutions of "$NaBH_2S_3$" with various organic species, which were reported as being different from those of $NaBH_4$ alone[21-24]. This so-called "Lalancette's Reagent" is now marketed by Aldrich as an intimate mixture of sulphur & $NaBH_4$ in a 3:1 ratio, to which it is recommended that THF is added to obtain a solution which should be used immediately.

Some work had already been carried out in this department on $LiBH_4$ complexes to investigate the metal-borohydride interactions[25]. The complex $LiBH_4$.TMEDA was found to exist as the dimer in the solid state, with the BH_4^- unit bonding through three of the H atoms, two μ_2 and one μ_3, with six-coordinate lithium atoms:

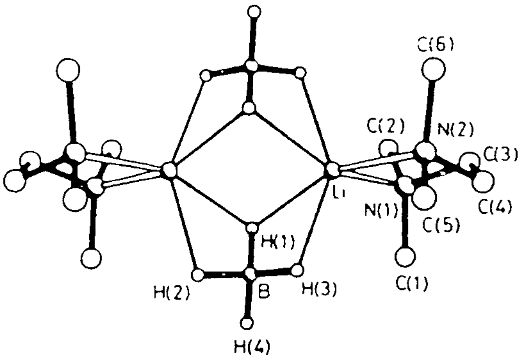


Fig. 6-VIII: The structure of the $LiBH_4$.TMEDA complex.

In the complex $LiBH_4$.PMDETA, by contrast, the BH_4^- binds to the lithium via two μ_2 bridges, and the lithium is five-coordinate due to the PMDETA ligand:

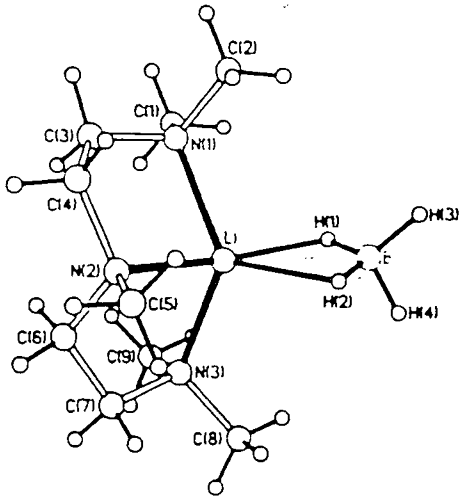


Fig. 6-IX: The structure of the $LiBH_4$.PMDETA complex.

Both structures were of interest in that in each the lithium is interacting with more H atoms of the borohydride than might have been expected from the octet rule. There was thus an interest in:

a) isolation and structural characterisation of the "$NaBH_2S_3$" species, or some derivative or complex thereof.

b) investigating whether any useful boron-containing species were formed by the reaction which could be used in the synthesis of carborane cages by building up smaller cages.

6.2 Experimental

$NaBH_4$ and $LiBH_4$ were used as received (Aldrich). Catechol was sublimed *in vacuo* prior to use and sulphur was dried in a desiccator over P_2O_5. All solvents were distilled over potassium. THF and monoglyme were stored over sodium and under dry N_2 and diglyme was stored under dry N_2 and away from strong sources of light. All manipulations involving Na/$LiBH_4$ were carried out in a glove box under an atmosphere of dry N_2 or on a vacuum line using standard Schlenk techniques.. All IR spectra of solids were taken using a nujol mull and KBr plates. Solution IR spectra were taken using a KBr solution cell, and gas phase spectra using a gas cell with KBr windows and a 10cm path length.

In a typical reaction with catechol, $NaBH_4$ was dissolved in the appropriate solvent in a 250ml flask. To this was added with stirring a solution of catechol in the same solvent via a dropping funnel. If the catechol did not dissolve in the solvent used, it was added as a dry powder via a rotatable tube. On reaction, there was a vigorous effervescence to produce a colourless gas.

In a typical reaction with sulphur, the borohydride was suspended in solvent in a 250ml three-necked round-bottomed flask with stirring under dry N_2. Sulphur was weighed into a bent glass tube which was then purged with dry N_2 and quickly fitted to the reaction flask. The sulphur was then slowly added to the stirred suspension to give a slightly exothermic reaction. A colourless gas was evolved and the solution became coloured. These solutions did not crystallise.

6.3 Reactions with 1,2-dihydroxybenzene

6.3.1 Reactions with a 1:1 $NaBH_4$:Catechol Ratio

Concentration and cooling of the solution of a reaction performed in THF yielded colourless, rhombohedral crystals. On drying in vacuo or under dry N_2, they became opaque and eventually disintegrated. A similar reaction with addition of TMEDA before crystallisation yielded apparently identical crystals which also disintegrated on drying.

Rhombohedral crystals without TMEDA:

M. Pt.: Charred slightly on heating to 331°C.

IR (cm^{-1}): Before exposure to air - 1590 (vw), 1487 (m), 1250 (m), 1200 (m), 1154 (w), 1120 (m, broad), 1098 (m), 940 (w), 912 (m), 793 (vw), 748 (w), 733 (m).
Same after exposure to air.

MS: EI - 91, 87, 85, 83, 77, 74, 71, 70, 69, 63, 59, 57, 56, 55, 48, 45, 44, 43, 42, 41 (100%), 39, 36, 31, 29, 28, 27.
CI^+ - 35 (100%), 33, 32, 31, 30, 29.

Analysis (%): Na 15.12, B 3.38, C 56.17, H 3.25, O 22.08.

NMR (^{11}B in diglyme): 14.72 ppm.

Rhombohedral crystals with TMEDA:

M. Pt.: Charred slightly on heating to 331°C.

IR (cm^{-1}): Before exposure to air - 1600 (w), 1483 (s), 1362 (m), 1291 (w), 1256 (m), 1235 (s), 1208 (m), 1132 (m), 1103 (s), 737 (s), 699 (m).
After exposure to air, the spectrum was identical to that of the crystals formed without the addition of TMEDA.

MS: EI - 116, 59, 58 (100%), 57, 56, 42, 30.
CI^+ - 117, 72, 58 (100%).

Analysis (%): Na 10.18, B 1.78, C 58.75, H 6.07, N 7.06, O 16.16.

NMR (^{11}B in diglyme): 14.63 ppm.

Concentration and cooling of the reaction solution in diglyme yielded no crystals. Attempted complexation of the species in solution with TMEDA was similarly unsuccessful. Removal of the solvent *in vacuo* produced a sticky residue which, when stirred in a little monoglyme for twelve hours at room temperature, produced a white precipitate.

White precipitate:

IR (cm^{-1}): Before exposure to air - 2300 (w), 2230 (vw), 1604 (w), 1491 (s), 1370 (m), 1238 (s), 1215 (m), 1100 (s, broad), 930 (m), 918 (m), 860 (m), 798 (w), 738 (s), 732 (s), 704 (m), 438 (vw).
After exposure to air - 1600 (w), 1497 (s), 1368 (m), 1257 (s), 1208 (s), 1150 (s), 1125 (s), 1103 (s), 1015 (vw), 915 (s), 798 (w), 732 (s), 703 (m), 440 (vw).

NMR (^{11}B in diglyme): -42.04, 8.58 & 14.49 ppm.

In monoglyme, reaction yielded an immediate white precipitate which was sparingly soluble in the monoglyme, as further crops of solid could be isolated on standing at room temperature. The solid was soluble in diglyme, THF and water to give colourless solutions which turned brown in air, and insoluble in toluene and hexane. Recrystallisation from THF yielded colourless, rhombohedral crystals which disintegrated on drying. A solution in distilled water in air yielded a grey/brown powder on evaporation. A similar solution under N_2 yielded colourless, plate-like crystals which turned grey/blue in air.

White precipitate:

M. Pt.: Charred slightly on heating to 331°C.

IR (cm^{-1}): Before exposure to air - 2390 (w), 1603 (w), 1238 (s), 1215 (m), 1151 (w), 1100 (s, broad), 1070 (s, broad), 1028 (m), 931 (m), 918 (m), 860 (m), 798 (m), 732 (s), 703 (m), 438 (w).
After exposure to air - 1600 (w), 1497 (s), 1259 (m), 1209 (m), 1152 (m), 1123 (m, broad), 1106 (m), 1017 (w), 918 (m), 798 (w), 733 (s), 706 (m), 440 (vw).

MS: EI - 60, 45 (100%).
CI^+ - 108 (100%), 91, 59, 58, 45, 44.

Analysis (%): Na 15.58, B 4.08, C 54.63, H 5.18, O 20.53.

NMR: (^{11}B in diglyme) -41.89, 8.53, 14.28 ppm.
(^{11}B in H_2O) 7.57, 13.05 ppm.
(^{11}B in H_2O at low pH) 19.39 ppm.
(^{13}C in H_2O at low pH) 116.0, 120.8, 143.4 ppm.

6.3.2 Reactions with a 1:2 $NaBH_4$:Catechol Ratio

Using diglyme as the solvent gave a similar reaction to the 1:1 case. Concentration and cooling failed to yield crystals, eventually producing a sticky residue. Stirring this with monoglyme produced a white solid.

White precipitate:

M. Pt.: Charred slightly on heating to 331°C.

IR (cm^{-1}): 1602 (w), 1491 (s), 1369 (m), 1247 (s), 1211 (m), 1118 (s), 1102 (s), 1010 (w), 918 (s), 864 (w), 798 (w), 733 (s), 700 (m), 430 (vw).

Analysis (%): Na 7.69, B 2.47, C 54.50, H 4.43, O 30.91.

NMR (^{11}B in diglyme): 14.38 ppm.

Note

None of the analyses fitted very well with the calculated values for the mono or bisdiol compounds or the starting materials. Expected for the monodioldihydrido complex:

Na 16.0, B 7.6, C 50.0, H, 4.2.

Expected for the bisdiol complex:

Na 9.2, B 4.4, C 57.6, H 3.2.

Many of the materials formed would be expected to be mixtures. Some were crystallised from THF and then lost solvent on drying, so an unknown amount of THF would still be complexed to the compound, producing a variable analysis.

6.4 Reactions with sulphur

6.4.1 Reactions using $NaBH_4$

The reaction of $NaBH_4$ with sulphur was carried out using the general reaction scheme given above, using diglyme as the solvent. This gave a green solution which slowly deposited a yellow precipitate over several days.

Yellow precipitate:

IR (cm^{-1}): 2290 (w), 2220 (w), 1263 (vw), 1128 (m), 1018 (m), 722 (w).

Analysis (%): Na 16.5, B 12.18, S 13.34.
Na:B = 0.6:1

Reaction in THF gave a stable yellow solution. Addition of TMEDA produced a deep red-brown solution from which precipitated a red-orange solid on standing.

Red-orange solid:

IR (cm^{-1}): 1660 (w), 1610 (w), 1155 (w), 1020 (w, broad), 730 (m).

MS: EI - 255, 192, 160, 128, 116, 96, 85, 71, 64, 58 (100%).
CI^+ - 117 (100%), 72, 58.

Analysis (%): Na 1.09, B 3.86, S 47.32, C 26.84, H 6.91, N 10.19.
C:N = 3:1, S:B = 4.2:1.

6.4.2 Analysis of Gaseous Reaction Products

A reaction was run using $NaBH_4$ in THF and the gases produced were swept through a cold trap at -196°C by a stream of N_2. No ring of condensed material was evident on the sides of the trap. The still frozen trap was connected to a gas phase IR cell via a vacuum line and evacuated. The system was sealed and the trap allowed to warm to room temperature. A pressure of only 5mmHg built up (corresponding to *ca.* 0.2 mmol of gas), and the IR spectrum showed no absorptions.

6.4.3 Reaction in the presence of Cyclohexene

20 mmol cyclohexene was added to the suspension of $NaBH_4$ before the addition of sulphur. This had no noticeable effect on the reaction. A portion of the solution was worked up using 40% NaOH and 30% H_2O_2 aqueous solutions. This solution was then flash vacuum distilled and the products analysed by gas chromatography. No evidence for the presence of cyclohexanol was found.

6.4.4 Reactions using $LiBH_4$

The general reaction method was used with THF as the solvent. Addition of TMEDA to a fresh reaction solution produced an orange colour, but no precipitate. Removal of solvent from a fresh reaction solution yielded a sticky yellow residue. Suspension of this residue in 30ml toluene and addition of 6ml (40 mmol) TMEDA with stirring at 60°C for two hours produced an orange solution from which a yellow solid rapidly precipitated. Concentration and cooling of the orange solution yielded cubic, orange crystals.

Yellow solid:

M. Pt.: 128°C (decomposes)

IR (cm^{-1}): 2370 (m), 1302 (w), 1239 (w), 1133 (w), 1100 (w), 1061 (w), 1013 (w), 1000 (w), 942 (w), 878 (w), 818 (m), 783 (w), 720 (w), 705 (w), 672 (w), 659 (w), 560 (w).

MS: EI - 192, 160, 128, 116, 96, 72, 64, 58 (100%), 42, 34.
CI^+ - 117 (100%), 72, 58, 46, 35 (100%).

Analysis (%): Li 2.08, B 8.06, S 31.18, C 28.59, H 7.46, N 10.80
C:N = 3:1, S:Li = 3.3:1, B:Li = 2.5:1, S:B = 1.3:1, C:Li = 8:1, N:Li = 2.6:1
Insoluble in benzene, toluene, THF or TMEDA.

Orange crystals:

IR (cm^{-1}): 2390 (w), 1292 (m), 1255 (w), 1180 (w), 1158 (w), 1132 (w), 1100 (w), 1068 (w), 1039 (m), 1023 (m), 950 (m), 790 (m), 772 (m), 730 (w), 582 (w).

MS: EI - 192, 160, 128, 116, 96, 72, 64, 58 (100%), 42, 30.
CI^+ - 192, 160, 117 (100%), 72, 58, 46, 35 (100%).

Analysis (%): Li 3.50, S 32.53, C 32.90, H 7.10, N 12.47
Calculated for Li_2S_6.2TMEDA: Li 3.2, S 43.8, C 32.9, H 7.3, N 12.8.
C:N = 3:1, S:Li = 2:1.

Does not dissolve in benzene, toluene, THF or TMEDA.

6.4.5 Gas Evolution Measurements

In a typical reaction 0.22g (10 mmol) $LiBH_4$ was suspended in 30 ml THF. This was then frozen using liquid N_2 and a tube containing 0.96g (30 mmol) sulphur was fitted to the flask under N_2 purge. The whole system was then evacuated and purged with N_2. After a final evacuation, the system was sealed. The sulphur was then added to the frozen suspension and the system allowed to warm slowly to room temperature with stirring. After the cessation of the reaction, the solvent was frozen again and the pressure in the system due to non-condensible gases was noted. As the volume of the system was known, the volume of gas evolved could be calculated.

S (mmol)	$LiBH_4$ (mmol)	S:Li Ratio	Volume gas (ml)	Vol. expected (ml)	Yield of available H (%)
47.3	94.6	2:1	187	2120	9
7.8	23.4	3:1	54	350	15
5.1	15.2	3:1	31	229	14
3.2	32.0	10:1	22	143	15
9.6	144.6	15:1	119	430	28
3.2	64.0	20:1	22	143	15

Table 5-I: Gas evolution data.

6.5 Discussion and conclusions

6.5.1 Reactions with Catechol

Initial reactions were carried out with a ratio of catechol: $NaBH_4$ of 1:1 in THF. This was done in the hope of obtaining a crystalline monocatecholato species. A crop of colourless, rhombohedral crystals was obtained which disintegrated on drying, and whose ^{11}B NMR signal in diglyme showed only one signal, at 14.6 ppm. In diglyme, the same reaction produced no crystals but three signals in the ^{11}B NMR, at 14.5, 8.6 & -42.0 ppm. The high field signal was due to BH_4^- (literature value -41.8 in diglyme[26]) and its presence indicated that the reaction did not proceed to a simple 1:1 catecholato complex as was hoped, the major product being the same as that in THF. A reaction run with a 2:1 catechol: $NaBH_4$ ratio gave just one signal, at 14.9 ppm. Thus it appeared that the major product in both cases was the 2:1 complex, with a small amount of another product present.

This was confirmed by the isolation of the product from the 1:1 reaction in diglyme by precipitation with monoglyme. Dissolution of this product in water gave a solution whose ^{11}B NMR spectrum showed two signals, at 13.0 & 7.6 ppm. These corresponded to the bisdiol complex and the monodiol dihydroxy complex respectively (lit. 13.3 & 7.9 ppm[13]). Acidification of this solution shifts the spectrum to a single signal at 19.4 ppm, corresponding to $B(OH)_3$ (lit. 19.5 @ pH 6.5[13], 19.9-18.8 in H_2O[27]), which is the stable species in acid solution. The ^{13}C NMR spectrum of this solution showed signals due to free catechol at 116.0, 120.8 & 143.4 ppm (lit. 115.8, 119.4 & 145.4 ppm[13]). If the monocatecholato dihydrido species were initially present at this stage, dissolution in water and acidification would presumably convert it into the dihydroxy species. However, the presence of the latter as the predominant species in aqueous solution cannot be taken as evidence of the former in aprotic solution, as the dihydroxy species forms from the biscatecholato complex in water.

Thus, the reaction between $NaBH_4$ and catechol in organic, aprotic solvents yields the biscatecholato anion almost exclusively, regardless of the initial reactant ratio. This is presumably due to the greater reactivity of the monocatecholato dihydrido borate (1-) intermediate initially formed towards catechol, making the species very difficult to isolate.

The monocatecholato dihydrido borate (1-) may account for the signal seen at 8.6 ppm in the ^{11}B NMR spectrum of the reaction in diglyme, but if so it was only present as a minor product, even though the BH_4^- was always present in excess.

Thus it appears that the desired monocatecholato dihydrido borate species $[BH_2O_2C_6H_4]^-$ was not obtained from the reaction of catechol and borohydride in organic, aprotic solvents. The major product from this reaction was the biscatecholato complex anion $B[O_2C_6H_4]_2^-$, far more conveniently prepared from catechol and $B(OH)_3$ in water.

6.5.2 Reactions with Sulphur

Early work was on the $NaBH_4$:S system with a reactant ratio of 1:3, using diglyme or THF as a reaction medium. The method used was modified from that of Lalancette[20]. He mixed the dry reactants and rapidly added the appropriate solvent, and these are the instructions given with the commercial "Lalancette's Reagent" mixture available from Aldrich. However, experiences in this laboratory showed that this method had a tendency to cause a violent reaction which would then distribute the products around the flask and up nitrogen lines, etc. Consequently, the method was adapted to allow the addition of one of the reactants, sulphur, as a solid to a solution or suspension of the particular borohydride used in the appropriate solvent. This was found to give a smooth, clean reaction with effervescence to give a coloured solution (green in diglyme, yellow in THF). Also, some control over the rate of reaction was possible by varying the rate at which the sulphur was added. However, no crystalline product was formed, even on the addition of the chelating ligand TMEDA.

There was initial interest in the possible production of useful boron-containing species which could be used in the build-up of boron hydride or carborane cages, enabling larger, more useful systems to be built up from the smaller, cheaper ones. However, IR analysis of the gases produced in this reaction indicated that no B-H species was produced. Also, the IR spectrum of a sample of flash vacuum distilled reaction solution showed only bands attributable to the solvent used. Confirmation of the absence of such boron hydride species came from reactions run in the presence of cyclohexene, a well known substrate for hydroboration reactions. The presence of boranes would have been shown by the hydroboration of the alkene and produced cyclohexanol on the subsequent work-up. No cyclohexanol was found.

The reaction involving $LiBH_4$ and sulphur was also studied by Lalancette *et al.*[20], so reactions were carried out in the 1:3 ratio in the hope of obtaining a crystalline lithium species. The reaction proceeded as for the $NaBH_4$ + sulphur case, producing a colourless gas and a yellow solution (in THF) which would not crystallise, even in the presence of TMEDA. Concentration of this solution produced a sticky yellow residue from which no further solvent could be removed. Suspension of this residue in toluene and addition of a four-fold excess of TMEDA with warming to 60°C for two hours produced an orange solution which quickly precipitated a yellow powder. Separation of this powder by filtration and concentration of the orange solution yielded a crop of cubic orange crystals. These were shown by X-ray diffraction to be the species $Li_2S_6.2TMEDA$. This has a structure containing an unbranched S_6^{2-} chain, each lithium being coordinated to each end of the chain and also to the two nitrogen atoms in the TMEDA molecule.

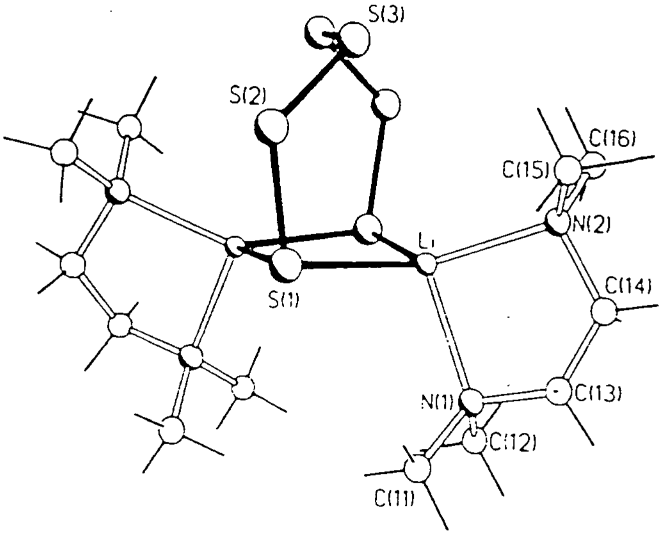


Fig. 6-X: The structure of the $Li_2S_6.2TMEDA$ complex.

In Durham, work had been performed on Li-S systems before in Dr. Banister's research group[28-30]. As lithium compounds are widely used as intermediates in organic synthesis, there is considerable interest in the structure and bonding in such compounds, both in the solid state and in solution. Li-S species had not, however, been widely studied. Several of the compounds studied in Durham proved to have novel and interesting structures. $(PhCOSLi.TMEDA)_2$ shows an eight-membered ring, $(COSLi)_2$, in the chair conformation, with the lithium above and below the COS plane. The compound is also predominantly ionic:

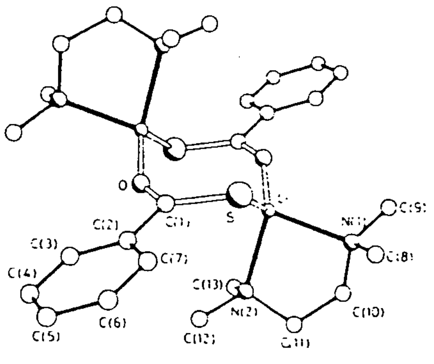


Fig. 6-XI: The structure of the $(PhCOSLi.TMEDA)_2$ complex.

Various lithium aryl thiolates, $ArSLi(py)_n$, where py is pyridine, adopt structures involving infinite $(LiS)_\infty$ chains and a buckled LiS ladder, where the Li-S bonds form the rungs, depending on the aryl group used:

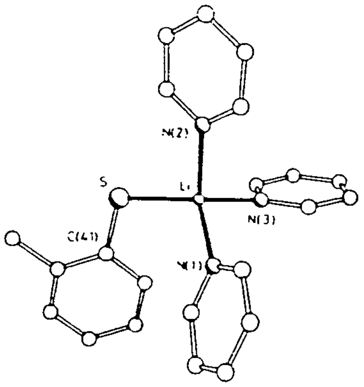


Fig. 6-XII: The structure of the $o-MeC_6H_4SLi.(py)_3$ complex.

Perhaps the most interesting is $Li_{14}(SCH_2Ph)_{12}S.(TMEDA)_6$. Its structure consists of a single sulphur atom at the centre of a distorted cube of lithium atoms; each of the twelve edges of the cube is bridged by an SCH_2Ph unit such that these twelve sulphur atoms form a cuboctahedron. Each pair of sulphur atoms is bridged by a Li.TMEDA unit, and these six lithium atoms form a huge outer octahedron:

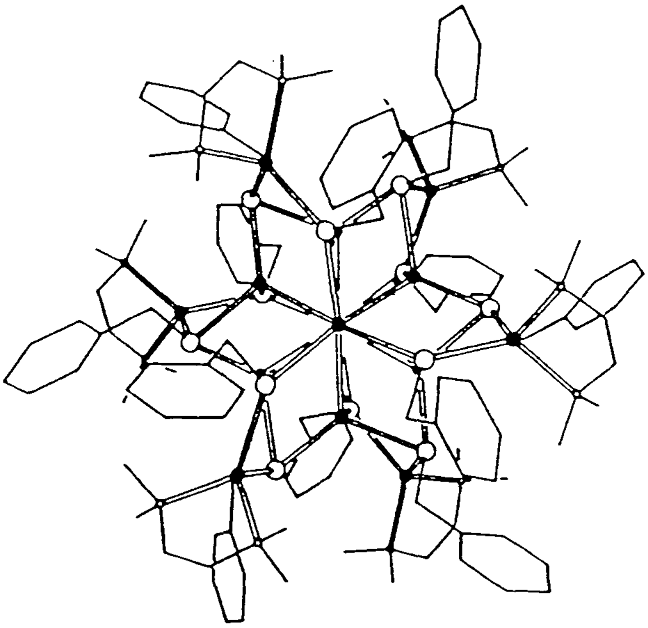


Fig. 6-XIII: The structure of the $Li_{14}(SCH_2Ph)_{12}S.(TMEDA)_6$ complex.

The formation of a lithium polysulphide as the only crystalline product of the reaction of $LiBH_4$ with sulphur was initially surprising, but it could help to explain some of the properties of "Lalancette's Reagent", as some of the reactions attributed to it can be explained by postulating a polysulphide as the reducing agent. Such species are well known in solution in a wide variety of aqueous, non-aqueous and organic solvents, e.g. H_2O[31,32], liquid NH_3[33], MeCN[34], DMSO[35], DMF[36], usually as a complex equilibrium of various anions and radical anions. These are generally formed by the chemical or electrochemical reduction of sulphur and are often highly coloured, e.g. the $S_3^{-\cdot}$ radical anion is a green colour. In solution S_n^{2-} with $n > 100$ have been reported[37], but in the solid state, generally $n < 7$.

Alkali metal polysulphides are well known in solution, but are less so in the solid state. Hexasulphides have been reported for Li[37], Na[38], K[39-41], and Cs[42] in solution, but only K_2S_6[39] and Cs_2S_6[42-44] have been isolated as crystals and structurally characterised. They were reported as free, uncomplexed species. Crystalline Na_2S_6 and Li_2S_6 have not been reported. However, recently a similar hexasulphide was prepared in which the alkali metal ions were chelated with cryptand ligands instead of bidentate TMEDA. This species was [K{cryptand(2.2.2)}]$_2$S$_6$[45], and was formed by the reaction:

$$K_2S_5 + S + \text{cryptand(2.2.2)} \longrightarrow [K\{\text{cryptand(2.2.2)}\}]_2S_6$$

However, the formation of this Li_2S_6 complex raised the question of what happened to the boron. Analysis of the yellow solid produced on addition of TMEDA showed that it contained B as well as Li, S, C, H & N. The C & N content was accounted for by the presence of complexed TMEDA, as C:N = 1:3. However, the material was not crystalline and did not dissolve to any extent in common solvents, thus being very difficult to crystallise or study by NMR. The analysis showed no definite stoichiometry and seemed to indicate that it was a mixture.

Thus the reaction between $LiBH_4$ and sulphur (1:3) was producing H_2, Li_2S_6 and a yellow solid product or mixture of products. The major reaction of sulphur with the B-H bond is the insertion of one or more sulphur atoms:

$$\mathrm{B{-}H} \quad + \quad [\mathrm{S}] \longrightarrow \mathrm{B{-}S{-}H}$$

$$\mathrm{B{-}H} \quad + \quad [\mathrm{S}]_n \longrightarrow \mathrm{B{-}[S]_n{-}H}$$

This has the effect of building up polysulphide units without evolution of hydride as H_2. Liberation of the H_2 could happen via condensation of an S-H unit with a B-H link:

$$\mathrm{B{-}H} \quad + \quad \mathrm{H{-}S} \longrightarrow \mathrm{B{-}S} \quad + \quad \mathrm{H_2}$$

H_2S may also be evolved *via* a similar mechanism:

$$\mathrm{B{-}SH} \quad + \quad \mathrm{HS{-}B} \longrightarrow \mathrm{B{-}S{-}B} \quad + \quad \mathrm{H_2S}$$

Hence such species as thioboric acid, $B(SH)_3$, and tetrathioborate(1-) $B(SH)_4^-$, could be produced. There is evidence for this type of process in the low temperature reaction of $LiBH_4$ with sulphur in diethyl ether (Et_2O) at -50°C, producing $LiBH_3(SH)$, which then reacts further on warming to produce $LiB_3S_2H_6$ and Li_2S with the evolution of H_2 at room temperature[19]. A process such as the condensation of thioboric acid to produce metathioboric acid, $(SBSB)_3$ which has a six-membered S_3B_3 ring, would not release all of the available H. Continuation of this process with further molecules of $B(SH)_3$ could produce the structure of B_2S_3, which consists of sheets of B_3S_3 six-membered rings and B_2S_2 four-membered rings, together with evolution of all of the available H as H_2.

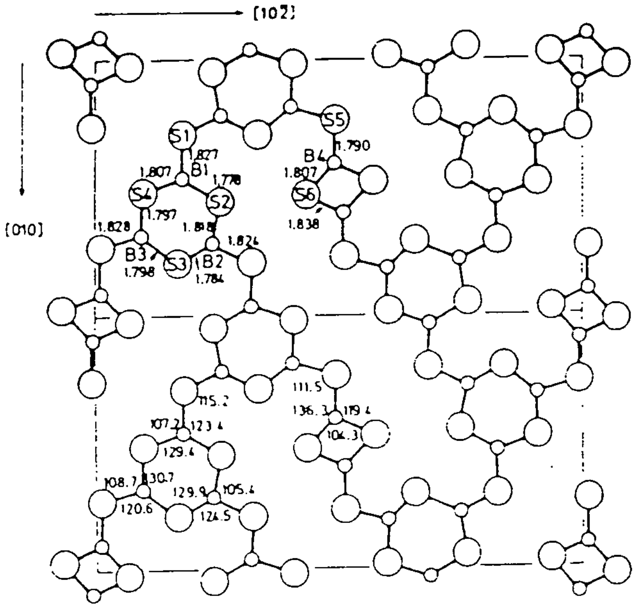


Fig. 6-XIV: The structure of B_2S_3.

From mass balance arguments, it is possible to set up a reaction scheme which involves the limiting cases of the least amount of sulphur necessary for complete evolution of H_2, and also the maximum amount of sulphur, assuming all the lithium to be converted into Li_2S_6 and all the boron to B_2S_3 with complete evolution of H_2.

The case of 3 sulphur atoms per $LiBH_4$ falls between these two cases:

$$LiBH_4 + 2\,S \longrightarrow 0.5\,Li_2S + 0.5\,B_2S_3 + 2\,H_2$$

$$LiBH_4 + 3\,S \longrightarrow 0.3\,Li_2S + 0.5\,B_2S_3 + 0.2\,Li_2S_6 + 2\,H_2$$

$$LiBH_4 + 4.5\,S \longrightarrow 0.5\,B_2S_3 + 0.5\,Li_2S_6 + 2\,H_2$$

This model predicts that the yield of $Li_2S_6.2TMEDA$ from the 3:1 reaction should be 40%, based on initial sulphur, and this was indeed found. However, it also predicts that all the boron is converted to B_2S_3 in the 4.5:1 case, and all the lithium to Li_2S_6 in the 2:1 case, and this was not observed. One major modification which needs to be made is to the assumption that all the available H is evolved as H_2. Gas evolution measurements indicated that only approximately 15% of available H is evolved, so most of the hydrogen must remain in the yellow product.

It seems that the reaction of $LiBH_4$ with sulphur is a complex process involving the insertion of sulphur into the B-H bonds of the borohydride with some evolution of the available H as H_2. There must also exist some mechanism for the formation of polysulphide anions. The complete identity of the yellow product has still to be established, but it seems very likely that it is a complex mixture of various Li/B/S species. The possibility that other polysulphide species, e.g. S_4^{2-}, may be formed also cannot be ruled out, as S_x is already known to react with S^{2-} to give S_{x+1}^{2-} anions[37].

6.6 References

1) e.g. AJ Hubert, B Hargity & J Dale; J. Chem. Soc., 1961, 931-6.
2) MJ Böeseken, MA Obreen & A Van Haeften; Rec. Trav. Chim., 1918, 37, 184-94.
3) PH Hermans; Z. Anorg. Chem., 1925, 142, 83-110.
4) J Meulenhoff; Z. Anorg. Chem., 1925, 142, 373-82.
5) J Dale; J. Chem. Soc., 1961, 922-30.
6) J Böeseken; Adv. Carbohydrate Chem., 1949, 4, 189-210.
7) PH Hermans; Rec. Trav. Chim., 1938, 57, 333.
8) Christ, Clark & Evans; Acta. Cryst., 1940, 62, 1529.
9) J Dale; J. Chem. Soc., 1961, 910-22.
10) H Sachse; Berichte, 1890, 23, 1363.
11) E Mohr; J. Prakt. Chem., 1918, 98, 315.
12) J Böeseken; Berichte, 1913, 46, 2612.
13) K Yoshino, M Kotaka, M Okamoto & H Kakihana; Bull. Chem. Soc. Japan, 1979, 52(10), 3005-9.
14) HC Brown, "Hydroboration", Benjamin, New York.
15) GW Kabalka, JD Baker & GW Neal; J. Org. Chem., 1977, 42(3), 512-7.
16) D Männig & H Nöth; J. Chem. Soc., Dalton Trans., 1985, 1689-92.
17) H Nöth & G Mikulashek; Allgem. Chem., 1961, 311, 241.
18) ZK Sterlyadkina, ON Kryukova & VI Mikheeva; Zh. Neorgan. Khim., 1965, 10, 10 & 583.
19) F Chopin & P Hagenmuller; Bull. Soc. Chim. France, 1965, 3031.
20) JM Lalancette, A Freche & R Monteux; Can. J. Chem., 1968, 46, 2754-7.
21) JM Lalancette, A Freche, JR Brindle & M Laliberte; Synthesis, 1972, 526.
22) JM Lalancette & A Freche; Can. J. Chem., 1969, 47, 739.
23) JM Lalancette & A Lachance; Can. J. Chem., 1969, 48, 859.
24) JM Lalancette & A Freche; Can. J. Chem., 1970, 48, 2366.
25) DR Armstrong, W Clegg, HM Colquhoun, JA Daniels, RE Mulvey, IR Stephenson & K Wade; J. Chem. Soc., Chem. Commun., 1987, 630-2.
26) H Noth & B Wrackmeyer, "NMR - Basic Principles and Progress. NMR Spectrometry of Boron Compounds", Vol. 14, Springer-Verlag, Berlin, 1978, p.395.
27) H Noth & B Wrackmeyer, "NMR - Basic Principles and Progress. NMR Spectrometry of Boron Compounds", Vol. 14, Springer-Verlag, Berlin, 1978, p.136
28) DR Armstrong, AJ Banister, W Clegg & WR Gill; J. Chem. Soc., Chem. Commun., 1986, 1672.

29) AJ Banister, W Clegg & WR Gill; J. Chem. Soc., Chem. Commun., 1987, 850.
30) AJ Banister, W Clegg & WR Gill; J. Chem. Soc., Chem. Commun., 1988, 131.
31) J Boulegue & G Michard; J. Fr. Hydrol., 1978, 9, 27-33.
32) A Teder; Ark. Kemi., 1969, 31, 173-98.
33) P Dubois, JP Lelieur & G Lepoutre; Inorg. Chem., 1988, 27, 73-90.
34) T Fujinaga, T Kuwamoto, S Okazaki & M Hojo; Bull. Chem. Soc. Japan, 1980, 53, 2851-5.
35) M Delamar; J. Electroanal. Chem., Interfacial Electrochem., 1975, 63, 339-49.
36) R Bonaterre & G Cauquis; J. Chem. Soc., Chem. Commun., 1972, 293-4.
37) RD Rauh, FS Shuker, JM Marston & SB Brummer; J. Inorg. Nucl. Chem., 1977, 39, 1761-6.
38) RP Martin, WH Doub, JL Roberts & DT Sawyer; Inorg. Chem., 1973, 12, 1921-5.
39) JM Letoffe, JM Blanchard, M Prost & J Bousquet; Bull. Soc. Chim. France, 1975, 148-60.
40) GJ Ganz, JW Coutts, JR Downey & E Roduner; Inorg. Chem., 1976, 15, 1755-9.
41) GJ Ganz & DJ Rogers; Proc. Electrochem. Soc., 1984, 84, 322-34.
42) SC Abrahams, F Grison & J Kalnajs; J. Am. Chem. Soc., 1952, 74, 3761.
43) SC Abrahams & E Grison; Acta. Cryst., 1953, 6, 206-13.
44) A Hardvik & AE Sletten; Acta. Chem. Scand., 1968, 22, 3029-30.
45) P Böttcher & H Buchkremer-Hermanns; Z. Naturforsch B, Chem. Sci., 1987, 42, 272-8.

CHAPTER SEVEN

7 Synthesis of some Substituted Acetylenes for Carborane Synthesis and an Investigation of a Novel Route to Carboranes

7.1 Introduction and Background

Carboranes are species consisting of a cage of boron and carbon atoms, the structure of which is generally composed of triangular faces. They are the neutral analogues of the deltahedral borane anions, $B_nH_n^{2-}$ (n = 6-12), utilising the fact that the CH unit is isoelectronic with BH^- to formally (though not practically) replace two BH^- units with two CH units. Structures consisting exclusively of closed cages are known as "closo" carboranes, and have a general formula $C_2B_nH_{n+2}$ (n = 3-10). The addition of two electrons to such a cage has the effect of opening the cage to a system in which the structure is based on a polyhedron with one more vertex than there are atoms in the cage, but with one vertex missing. These are known as "nido" cages. Addition of a further pair of electrons opens out the cage still further to a structure with two missing vertices, known as "arachno". These processes are due to the bonding in the structure which requires that the number of vertices in the *parent* structure is equal to one less than the number of electron pairs required for bonding. Thus, the addition of electron to a closo species increases the number of vertices in the parent structure, which for the same number of cluster atoms, must result in a missing vertex.

The closo carboranes have many properties in common with the borane anions, including their high thermal stability, but need no counter ions.

Also, the carbon atoms provide sites for the stable attachment of a huge range of groups, greatly expanding the range of chemistry available to these species. The incorporation of heteroatoms into the polyhedral framework also introduces the possibility of isomerism resulting from the positions of the heteroatoms relative to one another. For the closo carboranes, this is particularly important for $C_2B_8H_{10}$ and $C_2B_{10}H_{12}$. $C_2B_8H_{10}$, with its bicapped square antiprism structure, has seven possible isomers, though because carbon prefers sites of low connectivity, three are predominant: 1,2-, 1,6-, & 1,10-, with the latter being the most stable. As $C_2B_{10}H_{12}$ has only three possible isomers, and shows many similarities in its chemistry to that of benzene, these have been named ortho (1,2-), meta (1,7-), and para (1,12-).

The latter series of carboranes are those which have been most extensively studied, and are synthesised from decaborane(14), $B_{10}H_{14}$, with acetylenes in a donor solvent, e.g. Et_2S:

$$B_{10}H_{14} + 2\,Et_2S \longrightarrow B_{10}H_{12}.SEt_2 + H_2$$

$$B_{10}H_{12}.SEt_2 + RC{\equiv}CR \longrightarrow R_2C_2B_{10}H_{10} + 2\,Et_2S + H_2$$

This reaction yields the ortho isomer which, on heating to over 350°C, isomerises quantitatively to the meta isomer[1]. This adds a small amount of stability to the system as the carbon atoms are no longer adjacent, adding some more ionic character to the cluster bonding and relieving any steric strain between the substituents on the carbon atoms. However, heating to 600-650°C is required to form the para isomer in a low yield (~10%) process[2], as this temperature is close to the decomposition temperature of the carborane cage.

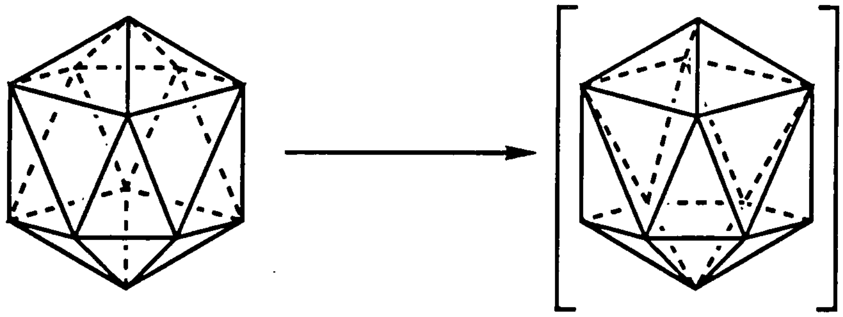
These carboranes have been incorporated, in the meta form, into siloxane polymers which are commercially available and are extremely thermally stable. The para isomer would provide modified polymer characteristics due to the greater linearity possible in the chains, but it is not widely available, for the reasons given above. If some way could be found to reduce the isomerisation temperature from meta to para, greater yields of the para carboranes would be available with consequent advances in high thermal stability polymer technology.

There have been many mechanisms proposed to explain the isomerisation of these species, the most prevalent being the "diamond-square-diamond" (DSD) mechanism. This was first proposed by Lipscomb *et al.* in 1962[3], and actually predated the observation of carborane isomerisation[1]. However, it explained the ortho to meta thermal isomerisation very well. It involves the stretching of six edges of the icosahedron to stretch the two triangular faces sharing that edge into a square face, thus yielding a cuboctahedral species. This can either rejoin the separated atoms, reverting to the original structure, or join the other two atoms in each square, thus forming a new isomer. This also has the effect of moving previously connected atoms from a 1,2- to 1,7- relationship, i.e. ortho to meta isomerisation. However, it cannot explain the meta to para change without being modified to include some rotation of the triangular faces of the cuboctahedral intermediate.

Lipscomb *et al.* put forward such a mechanism in 1967[4], involving weighted 120° rotation of faces, which went some way to explaining the observed results. Several other mechanisms were also proposed. One involved rotation of pentagonal halves of the cage in opposite directions ("pentagonal rotation mechanism") and was proposed by two sets of workers[1,5]. This can transform ortho to meta and meta to para in two steps, their relative ease being explained by the destabilising effect of adjacent carbon atoms on the ortho isomer, which is not present in the meta isomer. Another mechanism again involves the 120° rotation of triangular faces ("triangle rotation mechanism"), but this time in the icosahedral ground state of the molecule[5,6], and also explains the formation of the meta and para isomers from the ortho.

These various mechanisms were proposed in an attempt to explain the observed results of thermal isomerisation reactions, particularly those involving the use of labelled atoms. Each mechanism can explain certain results, but falls short for others, and may even fail entirely in some cases, e.g. DSD and meta to para isomerisation. However, none can satisfactorily explain both the presence and distribution of isomers observed in all isomerisation reactions, so there is still much work to be done in this field.

In 1989, Wu and Jones made a large step in this direction when they proposed their "extended triangle rotation" (ETR) mechanism for icosahedral carborane isomerisation[7]. In this they proposed that triangle rotation in the ground state molecule is the crucial step in the isomerisation reaction. However, in this case, the rotation is through 60° to create an intermediate in which two of the opposing triangles in the molecule are aligned the same way (see diagram over the page).



This intermediate then has four reaction pathways, one returning to the starting structure and the other three forming new structures, either by further rotation of the original triangle, or rotation of the triangle opposite it in the cage. This mechanism effectively incorporates within it both the DSD and triangle rotation mechanisms as subsets, as it can be shown that by the ETR route, the products of both of these mechanisms arise from a common reaction intermediate. The system also goes some way to explaining some hitherto anomalous experimental results.

One last mechanism, proposed by Lipscomb & Wong in 1975[8] involves the opening of the closo structure to a nido cage based on a 13 vertex polyhedron, closure of which in a different way leads to isomerisation of the original carborane. This mechanism is expected to apply to systems under reducing conditions, the closo->nido conversion requiring an extra pair of electrons.

We can see that there are many and various mechanisms available for this much-studied reaction, but one thing they all hold in common, by definition, is that they all depend on the ease, or lack of it, with which the cluster atoms can move relative to each other. This, in turn, depends to some extent on the bonds holding the atoms together; their strength and flexibility.

However, it is sometimes misleading to speak of the bonds in clusters such as $C_2B_{10}H_{12}$, as the traditional 2c2e bonding models tend to fall down, as we have seen. Also, the way that icosahedral carboranes are usually depicted, that is showing the *structure* of the cluster primarily, can often lead to confusion that the *edges* of the icosahedral *structure* represent *bonds* between atoms in the cluster. If this were so, then the structure would be extremely rigid and very difficult to isomerise at all. In reality, the bonding picture is much more flexible than this, as we have seen, involving 3c2e bonds and MOs which encompass the whole cluster.

It would be reasonable to assume that changing the electronic characteristics of the cluster would have an effect on the bonding within it, and consequently on the isomerisation of the cluster. We have seen that the addition of electrons to a cluster has the effect of opening it out, and their removal has the effect of closing it up. Thus, adding electrons to, in effect reducing, a nido cluster would open it out into an arachno cluster, whereas removing electrons from it, in effect oxidising it, would form a closo cluster. Such an effect could perhaps be observed by the effect of substituents on a carborane on the ease of isomerisation of the cluster; electron withdrawing substituents may make the cluster close up, whereas electron donating substituents may make it open up slightly, loosening the framework a little, so making isomerisation a little easier. After all, one mechanism for the reaction, that has been exploited experimentally, involves a formal opening of the closo structure to a nido form followed by reclosure.

Many of the carborane derivatives studied have been dialkyl species, so there are many examples of systems containing two electron donating groups, e.g. dimethyl carborane. There was thus an interest in preparing derivatives with two electron withdrawing groups, e.g. bis(pentafluorophenyl) carborane, in order to compare the isomerisation reactions of the two systems. These are best synthesised from $B_{10}H_{12}L_2$ with the appropriate disubstituted acetylene, so some representative examples of these species were prepared.

As we have seen, the $B_{12}H_{12}^{2-}$ borane anion is highly thermally stable, as is the corresponding carborane, $C_2B_{10}H_{12}$. However, the most stable of its three isomers, the 1,12- or para isomer, is difficult to obtain in high yield due to the severe conditions required for the usual thermal isomerisation route. One way to increase the yield of this product would be to lower the temperature required for this route, as outlined above. Another way would be to try a completely different synthetic route altogether. It was this approach which led to the suggestion that reactions of the $B_{10}H_{10}^{2-}$ cage might lead to carborane species.

The normal method of attack on such cages is by electrophilic reagents to yield substitution products by replacement of the exopolyhedral groups. However, such attack by electrophiles would tend to draw electron density from the cage, causing it to close up, and reducing the chance of any insertion into the cage. If an electron-rich species could be induced to attack the cage, the electron density it would provide might be sufficient to loosen the cage structure enough for an atom to insert into the structure of the cluster. Such a species would need to be extremely reactive in order to overcome the large energy barrier there would be to such a reaction between two electron-rich species. Such a group may be a carbene.

Experiments were carried out in an attempt to react a carbene with the $B_{10}H_{10}^{2-}$ cage, and the results were analysed by ^{11}B NMR. The borane compound used was bis(triethylammonium) decaborane (10) $[Et_3NH]_2B_{10}H_{10}$, and the source of carbene was the thermal decomposition of sodium trichloroacetate:

$$CCl_3CO_2Na \longrightarrow NaCl + CO_2 + :CCl_2$$

7.2 Preparation of Disubstituted Acetylenes with two Electron Withdrawing Groups

7.2.1 Preparation of Bis(4-pyridyl)acetylene

5.01g (27.5mmol) trans-1,2-bis(4-pyridyl)ethylene were suspended in 100ml 48% aqueous HBr in a 500ml round bottomed flask. This stirred suspension was cooled to 0°C (ice/water bath) and 15.4g (5.0ml, 193mmol) Br_2 was added dropwise with vigorous stirring. The colour of the suspended solid turned from white to orange. After the completion of the addition, the suspension was heated to 120°C with stirring for one hour before being cooled to 0°C and filtered to remove the orange solid. This was then stirred in 2M NaOH solution until the colour remained constant (pale yellow), and the solid was again filtered off and dried *in vacuo* (7.45g, 79% yield at this stage).

A solution of 1.4g (61mmol) Na was made up in 150ml hot ^tBuOH and was then refluxed while a suspension of 5g of the bromo derivative in 80ml ^tBuOH was added with stirring, after which reflux was continued for a further 30 minutes before the solution was allowed to cool to room temperature. Some of the solvent was then removed *in vacuo* to leave ~80ml, and ~2ml water was added with stirring. The remainder of the solvent was then removed under reduced pressure to give a yellow solid which was extracted with diethyl ether in a soxhlet apparatus, and the resultant yellow solution was evaporated to dryness to yield a yellow crystalline solid (2.52g, 95% yield on the last step).

M. Pt.: 114-6°C (lit. 114°C, uncorrected[9]).

7.2.2 Preparation of Diiodoacetylene (C_2I_2) (starting material)

A solution of 9.95 85% KOH (~150mmol) in 300ml water was made up in a 500ml round bottomed flask fitted with a mechanical stirrer and sintered glass inlet tube. The large size of the flask was found to be necessary to provide sufficient volume for efficient stirring of the suspension formed in the reaction. 32g (125mmol) I_2 and 35g (210mmol) KI was dissolved in 50ml water and added dropwise with vigorous stirring to the KOH solution, while C_2H_2 was bubbled through the solution. Stirring was at such a rate that the KI/I_2 solution was decoloured after one revolution round the flask, although addition of further KOH was sometimes necessary to achieve this. The C_2I_2 formed as a white, waxy precipitate which floated on top of the solution. After completion of the addition of the KI/I_2, the solid was filtered off and washed with water before being dried and placed in a desiccator away from light. The solid was sensitive to light (turning brown on prolonged exposure) and had a characteristic, pungent smell.

Yield = 12.1g (35%)

7.2.3 Preparation of Bis(pentafluorophenyl)acetylene

A dry 250ml round bottomed flask fitted with a condenser was charged with Mg (1.32g, 54mmol) under an atmosphere of dry nitrogen. 100ml dry Et_2O was added and the system cooled to -20°C (dry ice/acetone bath) before the addition of C_6F_5I (6.7ml, 14.7g, 50mmol) with stirring. The mixture was allowed to warm to ~0°C until reaction commenced, and the reaction was then controlled by the temperature of the cooling bath. This produced a brown solution of the Grignard reagent. Anhydrous $CoCl_2$ (0.60g, 7mmol, dried @ 150°C *in vacuo* for 4 hours) was added to the cold (-20°C) solution under nitrogen flow to give a blue solution on stirring. A solution of C_2I_2 (6.95g, 25mmol) in dry 50ml Et_2O was added to the stirred solution at -20°C via a dropping funnel. After completion of addition, the solution was stirred at -20°C for an hour and then allowed to warm to room temperature under nitrogen, with stirring continued for a further 16 hours.

50ml of a 20% solution of acetic acid in water was then added with stirring at a rate sufficient to reflux the Et_2O solvent. After cooling, the brown solution was washed with water (4 x 100ml), dried with $MgSO_4$, filtered, and the solvent removed under reduced pressure to yield a brown solid. This was dissolved in hot 60-80 petroleum ether and cooling produced crops of translucent brown crystals. These were purified by sublimation (60°C, 0.005mmHg).

Yield = 7.67g (crude), 86%

Sublimation yielded an 82% recovery of pure material.

Elemental analysis: C 46.69, F 52.84.

$C_{14}F_{10}$ requires: C 46.95, F 53.05.

7.2.4 Attempted preparation of Bis(pentafluorophenyl)acetylene by modification of a literature method[10]

A dry 250ml round bottomed flask was fitted with a sintered glass bubbler and charged with a catalytic amount of $(PPh_3)_2PdCl_2$ (73mg, 0.1mmol), together with sufficient Et_2NH to cover the sinter (100ml). C_6F_5I (1.3ml, 20mmol) was then added and the solution stirred for a few minutes. A small amount of CuI (12mg, 0.06mmol) was added and C_2H_2 bubbled slowly through the stirred suspension. After an hour, the solution turned red/brown and cloudy. After 23 hours, the solution was dark red/brown and all solids had dissolved. The Et_2NH was removed *in vacuo* and 100ml distilled water was added with stirring. The resultant solution was extracted with toluene (5 x 50ml), and the toluene removed from the washings under reduced pressure to produce a sticky red/brown residue. Dissolution of this in di-^{n}butyl ether yielded a red solution and a brown solid. However, attempted recrystallisation of this from 60-80 petroleum ether failed to yield satisfactory samples of the target acetylene.

7.3 Investigation of Novel Routes to Carboranes

7.3.1 Reaction of $[Et_3NH]_2B_{10}H_{10}$ with CCl_3CO_2Na

Blanks were run on both reagents to use as a reference when interpreting the results. A range of conditions was chosen to vary reactant ratio, reaction time and reaction temperature. Diglyme was the usual solvent, though DMF was also used for the first run, as there was some concern over the large heat of dissolution of CCl_3CO_2Na in diglyme. However, this was not observed, and diglyme was adopted as the standard solvent. Solvents were dried and stored under nitrogen. $(Et_3NH)_2B_{10}H_{10}$ was purified by recrystallisation from water and CCl_3CO_2Na was used as received.

In a typical reaction, 1.61g (5 mmol) $[Et_3NH]_2B_{10}H_{10}$ was placed in a 100ml two-necked, round-bottomed flask with 3.70g (20 mmol) CCl_3CO_2Na. 50ml solvent was added and the mixture stirred at room temperature until the CCl_3CO_2Na had dissolved. The flask was then fitted with a thermometer and a condenser and heated with stirring (magnetic follower). At ~80°C, effervescence commenced, and heating was continued to reflux and maintained for ~20 hours (~150°C). After cooling, the solution was filtered to yield a fawn/brown solution and a sticky fawn/brown solid. This was dissolved in distilled water and analysed by ^{11}B NMR.

7.3.2 Results

Summary of Reactions

Solvent	CCl_3CO_2Na: $B_{10}H_{10}^{2-}$ ratio	Temperature (°C)	Reaction time (hours)
DMF/diglyme	8	150	2
diglyme	4	150	24
diglyme	3	100	24
diglyme	6	150	60
diglyme	CCl_3CO_2Na	150	5
diglyme	$(Et_3NH)_2B_{10}H_{10}$	150	3

Summary of ^{11}B NMR Data

Run 1: δ: -29.8d, -0.8d

Run 2: δ: -29.8d, -0.8d, 5.8s, 25.4d

Run 3: δ: -29.8d, -24.8d, -0.8d, 3.9s

Run 4: δ: 17.6s

$(Et_3NH)_2B_{10}H_{10}$ blank: δ: -29.8d, -0.8d, 18.9s

Summary of ^{13}C NMR Data

Run 2: δ: 6.9 (Et_3NH), 46.1 (Et_3NH), 55.5, 57.9 (diglyme), 69.2 (CCl_3CO_2Na), 70.8 (diglyme), 165.4 (CCl_3CO_2Na).

Runs 3 & 4 showed the same signals.

Elemental Analysis Summary

Run 1: Na 36.33, Cl 49.22, B 1.99, C 1.43, H 0.25, N 0.00

CCl_3CO_2Na blank: Na 36.80, Cl, 57.64, C 1.85, H 0.23.

NaCl requires: Na 39.3, Cl 60.7.

7.4 Discussion

The initial purpose of synthesising the above acetylenes was to inorporate them into a $C_2B_{10}H_{12}$-type icosahedral carborane structure by the method outlined above (via $B_{10}H_{12}L_2$) and then study the temperature of the ortho to meta isomerisation. However, time did not allow the continuation of this work, as the priority was the synthesis of derivatives of the brominated alcohol and diol as described previously. The routes to such disubstituted acetylenes could be further developed and modified to produce more examples containing two electron withdrawing groups. Also, species with two strongly electron donating groups could be prepared so comparison of the isomerisation temperatures of the target carboranes could be made. Acetylenes combining both electron withdrawing and electron donating groups may also be of interest in this area. However, these groups may also affect the ease of formation of the target carboranes.

Such a study of the relative isomerisation temperatures of these three types of carborane would be of great interest. If it proved to be the case that isomerisation to the 1,12 isomer could be achieved at significantly lower temperatures than was possible before, this may have great benefits for high temperature polymers and their applications.

The ^{11}B NMR spectrum of the first, the shortest run with $B_{10}H_{10}^{2-}$ and $:CCl_2$ showed the peaks due to $B_{10}H_{10}^{2-}$ at -29.8 & -0.8ppm. It also showed several peaks in the 0 to -40ppm range which were not well defined and rose from a general broad background band. Continuing the reaction for a longer time as in the second run simplified the spectrum somewhat. Peaks due to the starting material were still present, as well as a signal at 5.8ppm (singlet) and one at -25.4ppm (doublet, J ~ 100Hz), together with another broad set of unresolved signals from 0 to -10ppm. The peak at -5.8ppm can be ascribed to borate, $B(OH)_3/B(OH)_4^-$, which has a resonance in the range 1 to 20ppm, depending on the pH of the solution. A signal at ~6ppm indicates a fairly alkaline solution. That leaves the signal at -25.4ppm and the signals around -5ppm to assign.

The third run showed a very similar spectrum, with a borate signal at -3.9ppm, a broad band at -24.8ppm (doublet, not well resolved), and some signals between 0 and -5ppm which seemed to split into doublets on coupling (J ~ 100-130Hz), but were not very well resolved. The predominant species present was $B_{10}H_{10}^{2-}$, the borate peak being comparatively weaker than in the second run, due perhaps to the less severe conditions used. The fourth run, for 60 hours, showed only one signal in its ^{11}B NMR spectrum, at 17.6ppm, a singlet due to borate. This indicates complete degradation of the $B_{10}H_{10}^{2-}$ cage into species which yield $B(OH)_3$ on dissolution in water. Degradation of the cage into smaller borane anions or boranes would decrease the hydrolytic stability of the system, the lower boranes and borane anions hydrolysing to give $B(OH)_3$ and H_2.

The blank reaction of $B_{10}H_{10}^{2-}$ heated in diglyme showed signals due to $B_{10}H_{10}^{2-}$ together with a strong signal at 18.9ppm due to borate. However, there was also an increase in signal intensity peaking at -5 and -25ppm. These appeared to be the same signals that appeared in the reactions with CCl_3CO_2Na.

The ^{13}C NMR spectra of the second and third reaction solutions in water were virtually identical. That of the fourth run was much weaker, but showed essentially the same peaks, together with some minor signals in the 50-70ppm region, probably due to decomposition products from the prolonged heating of the sample. The only major unassigned peak appeared at 55ppm.

Analysis of the solid product of the first reaction showed it to be ~85% NaCl with only ~2% boron and ~1.5% carbon. Isolation of a solid product from subsequent reactions was precluded by the resinous nature of the products.

The blank run with CCl_3CO_2Na yielded a product which was shown by the elemental analysis to be ~95% NaCl

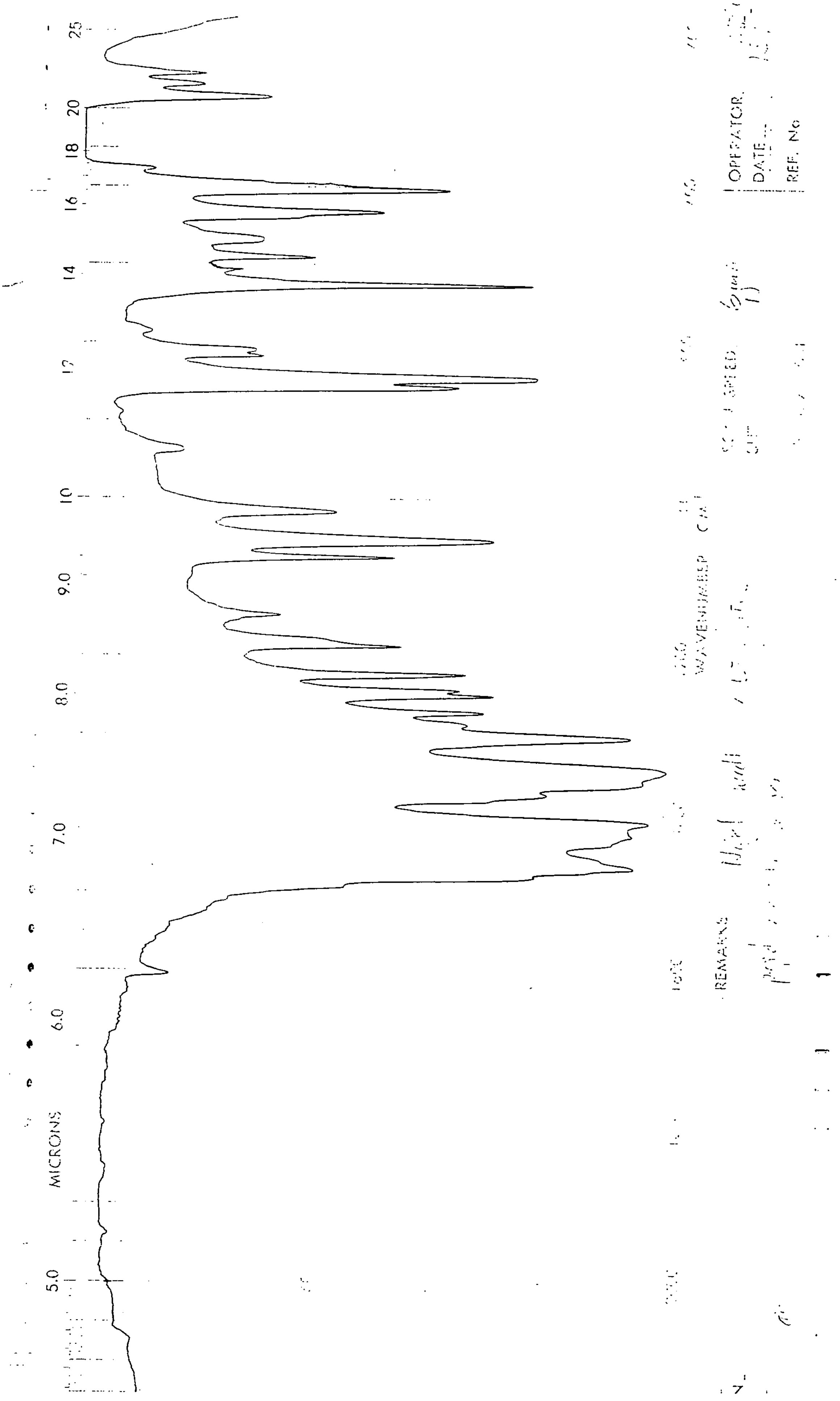
There are several possibilities for the products of insertion of carbon into the $B_{10}H_{10}^{2-}$ cage. The most desirable products, i.e. C_2B_{10} icosahedral carboranes, could be obtained. The ortho, meta and para forms of this carborane contain four, four and two boron environments, respectively. Incorporation of one carbon unit into the cage to give a closo CB_{10}^{-} eleven vertex structure would also give at least four boron environments, even for the most symmetrical isomers. A one carbon CB_{10}^{3-} species based on an icosahedron would have either two or six boron environments. Evidence for such signals in the ^{11}B NMR spectra of the products obtained from the above reactions is lacking. Some of the signals observed are in the right region of the spectrum for icosahedral carboranes, but they are very badly defined, and could also be due to other BH-containing species. Also, the same signals were seen on the blank run with no CCl_3CO_2Na present, so this would seem to preclude carborane formation.

Thus it appears that when $B_{10}H_{10}^{2-}$ is heated at 150°C in diglyme with CCl_3CO_2Na, $:CCl_2$ is produced and the $B_{10}H_{10}^{2-}$ cage decomposes to give smaller fragments, possibly lower borane anions or boranes, the decomposition being essentially complete after 60 hours. However, incorporation of carbon into the boron cage does not seem to take place, a blank run with no CCl_3CO_2Na giving similar results to the runs with CCl_3CO_2Na. The$B_{10}H_{10}^{2-}$ decomposition products give ^{11}B NMR signals at ~-4 and ~-25ppm, both signals being doublets.

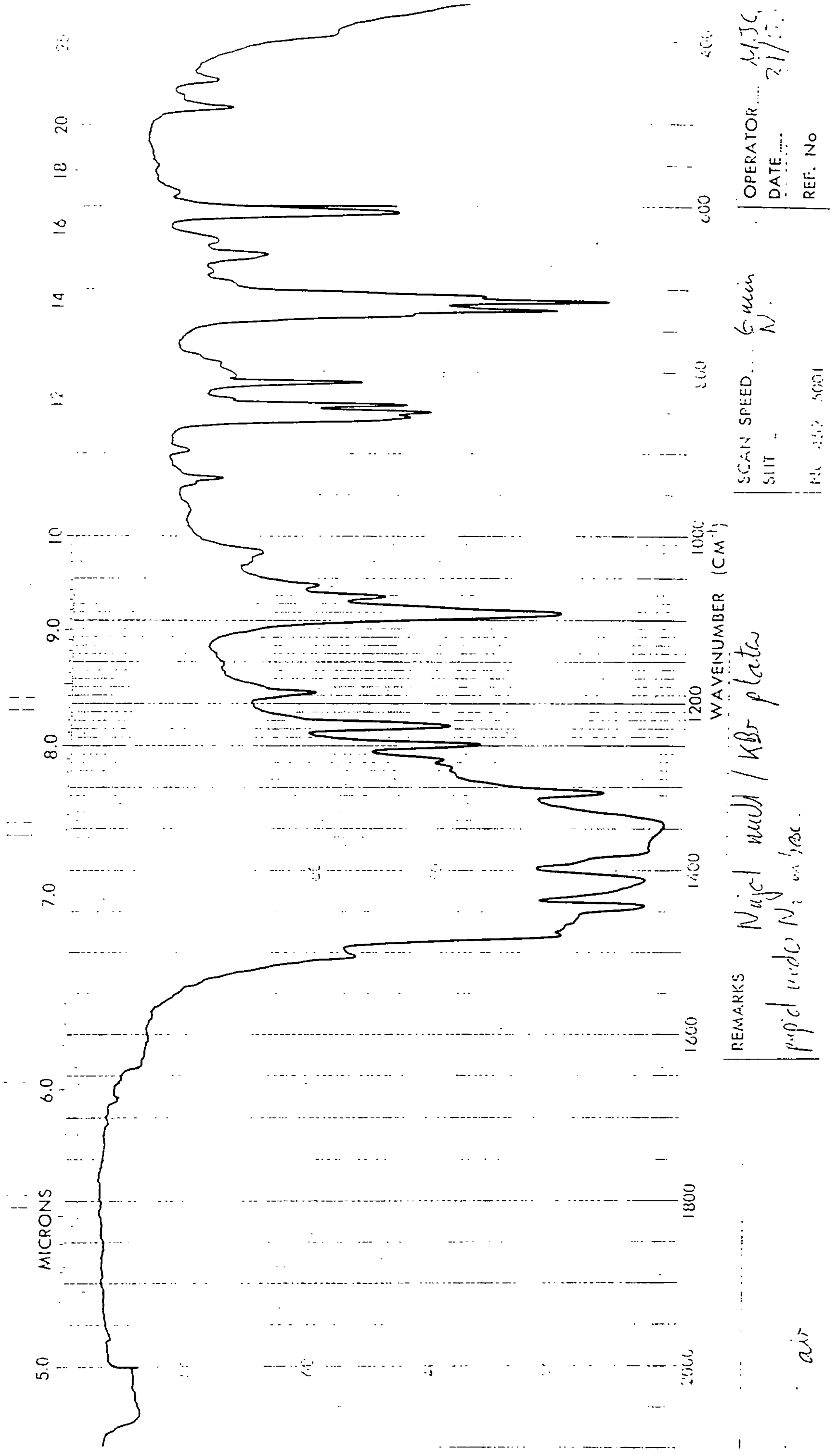
7.5 References

1) D Grafstein & J Dvorak; Inorg. Chem., 1963, 2, 1123.
2) S Papetti & TL Heying; J. Am. Chem. Soc., 1964, 86, 2295.
3) A Kaczmarczyk, RD Dobrott & WN Lipscomb; Proc. Nat. Acad. Sci. USA, 1962, 48, 729.
4) HD Kaesz, R Bau, HA Beall & WN Lipscomb; J. Am. Chem. Soc., 1967, 86, 4218.
5) LI Zhakharkin & KN Kalinin; Dokl. Akad. Nauk. SSSR, 1966, 169, 590.
6) EL Muetterties & WH Noth; "Polyhedral Boranes", Marcel-Dekker, New York, 1968, p.55.
7) S Wu & M Jones; J. Am. Chem. Soc., 1989, 111, 5373-5384.
8) HS Wong & WN Lipscomb; Inorg. Chem., 1975, 14, 1350.
9) M Tanner & A Ludi; Chimia, 1980, 34(1), 23-4.
10) K Sonogashira, Y Tohda & N Hagihara; Tetrahedron Letters, 1975, 50, 4467-70.

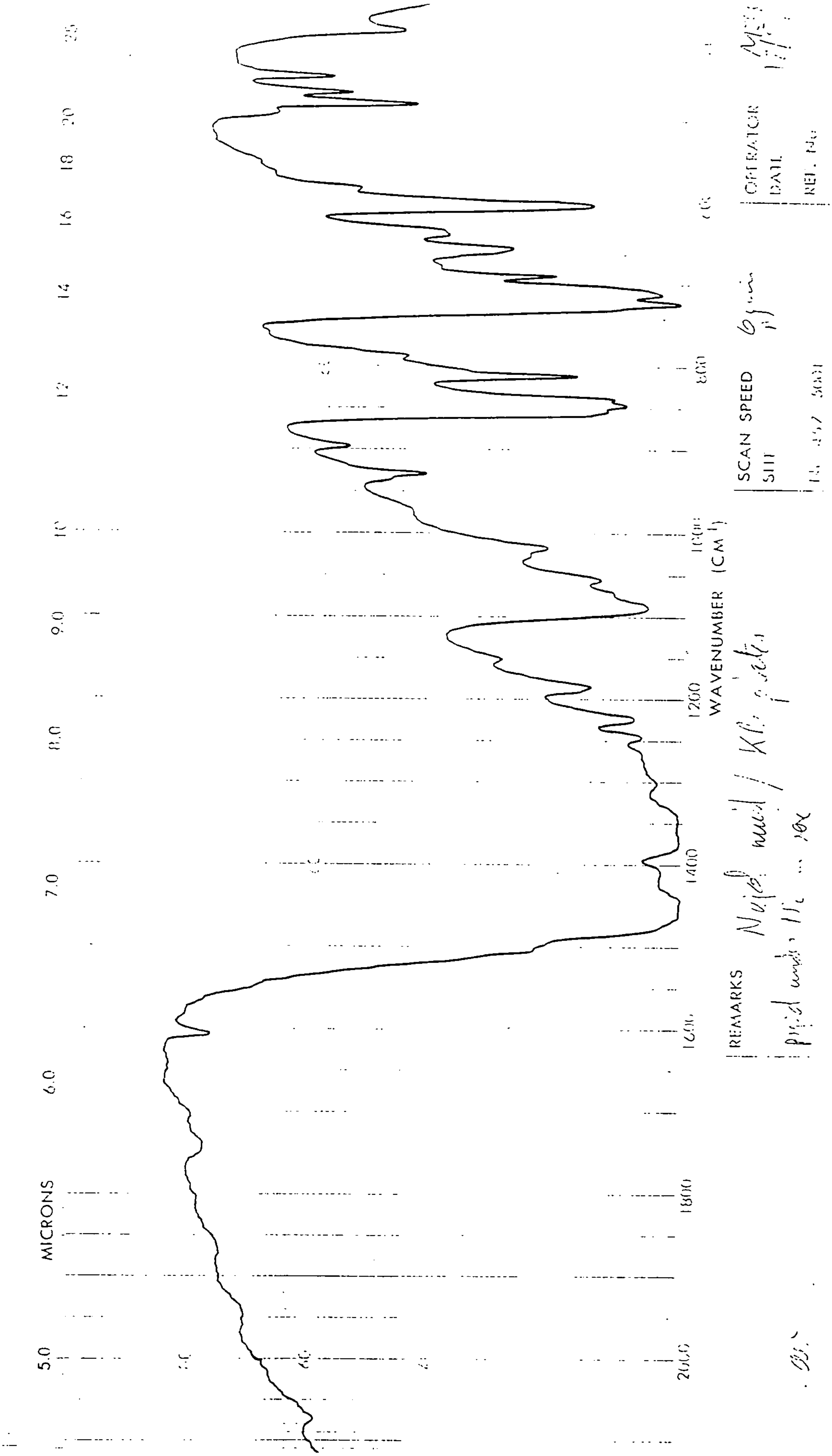
APPENDIX A



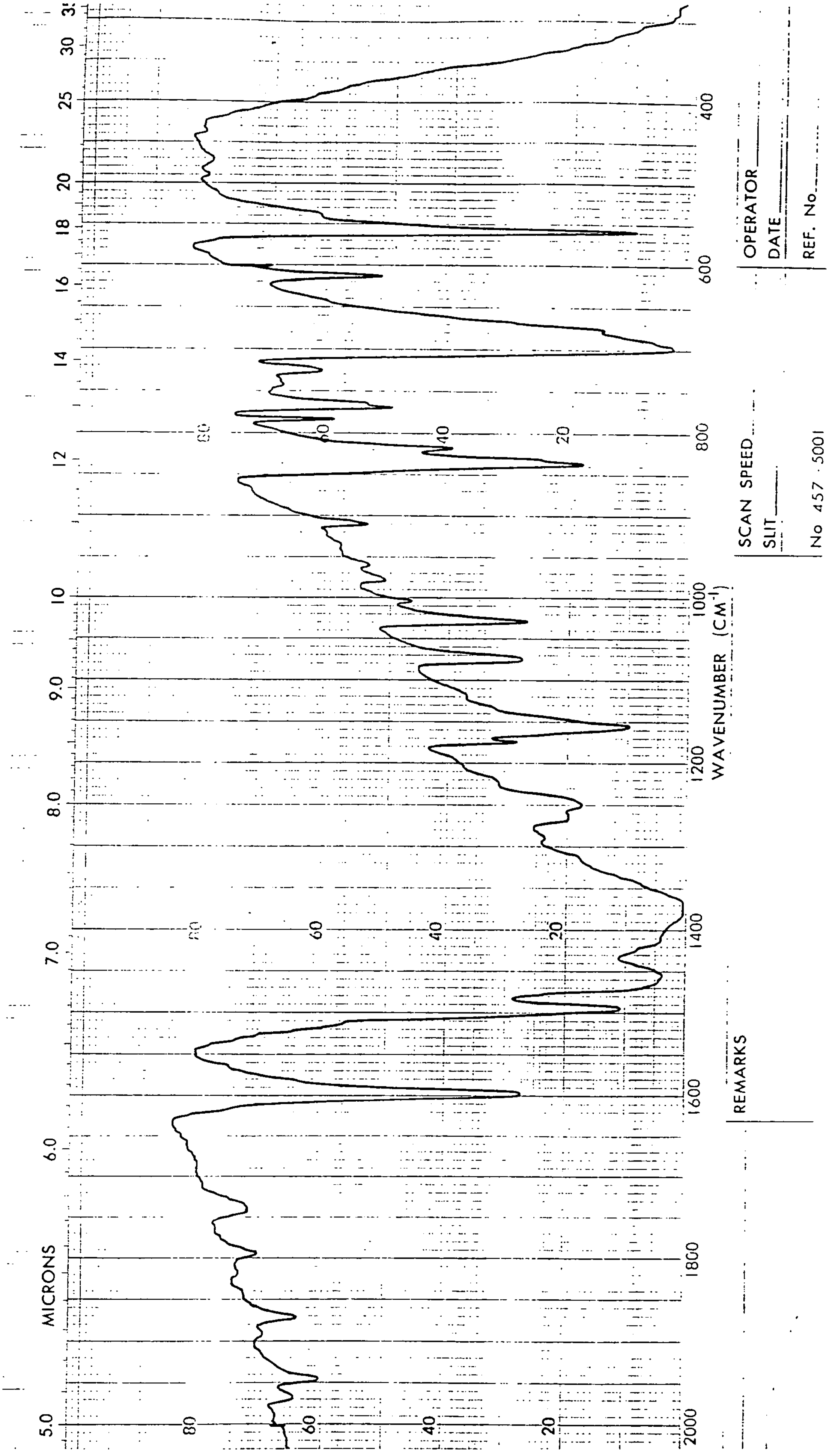
IR spectrum of B(OTBN)3



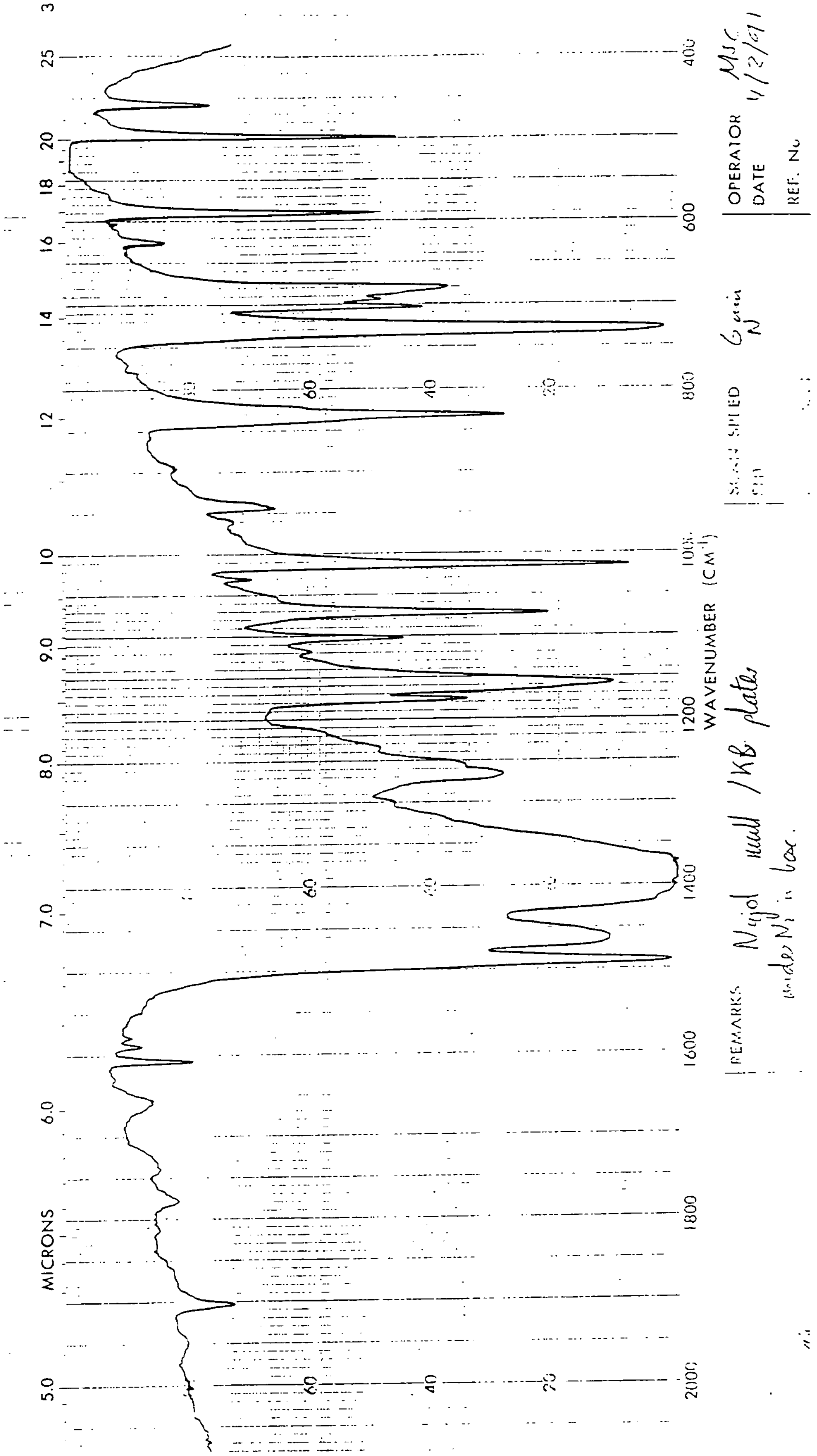
IR spectrum of $(TBNOBO)_3$



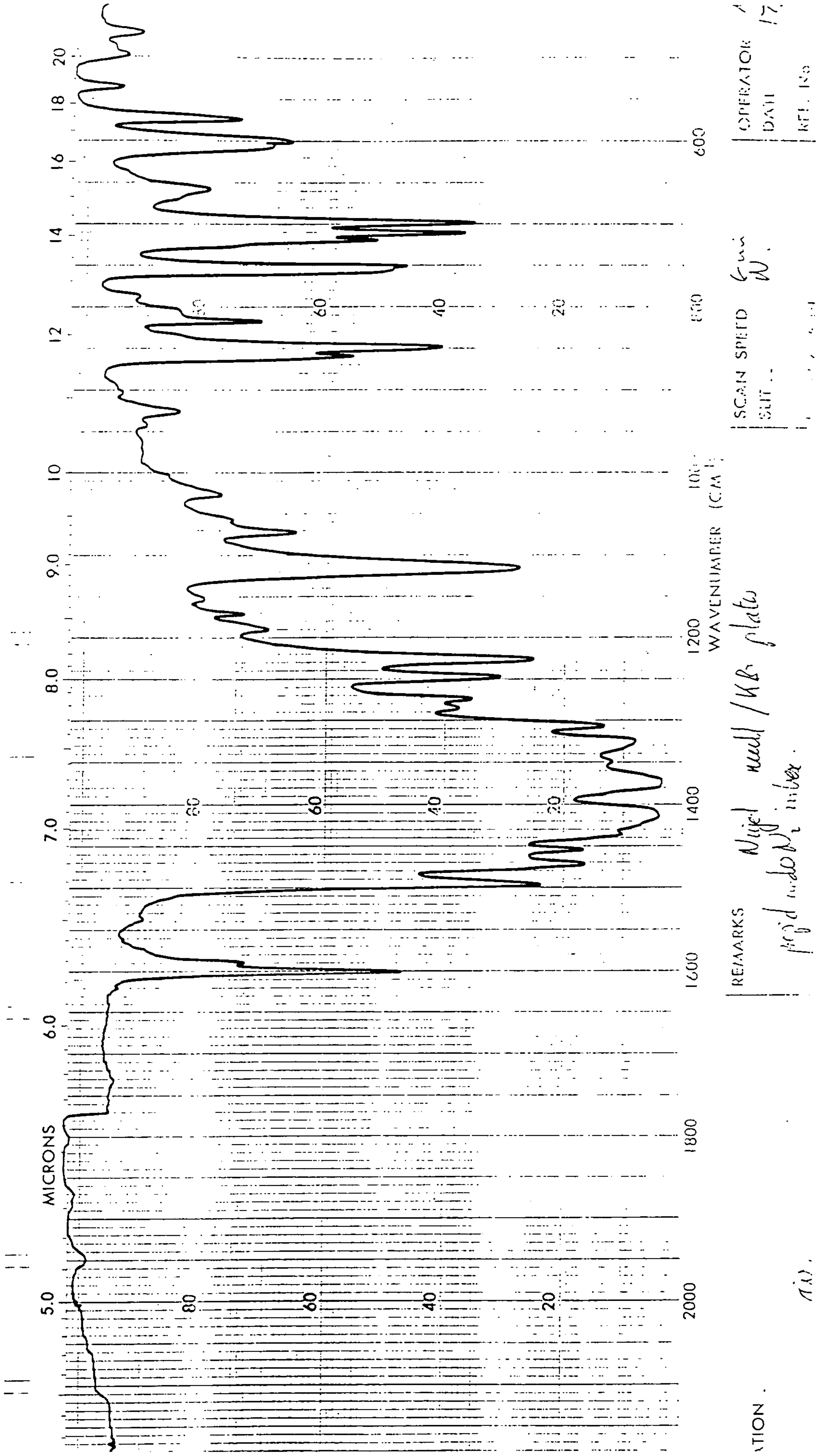
IR spectrum of Polyborate



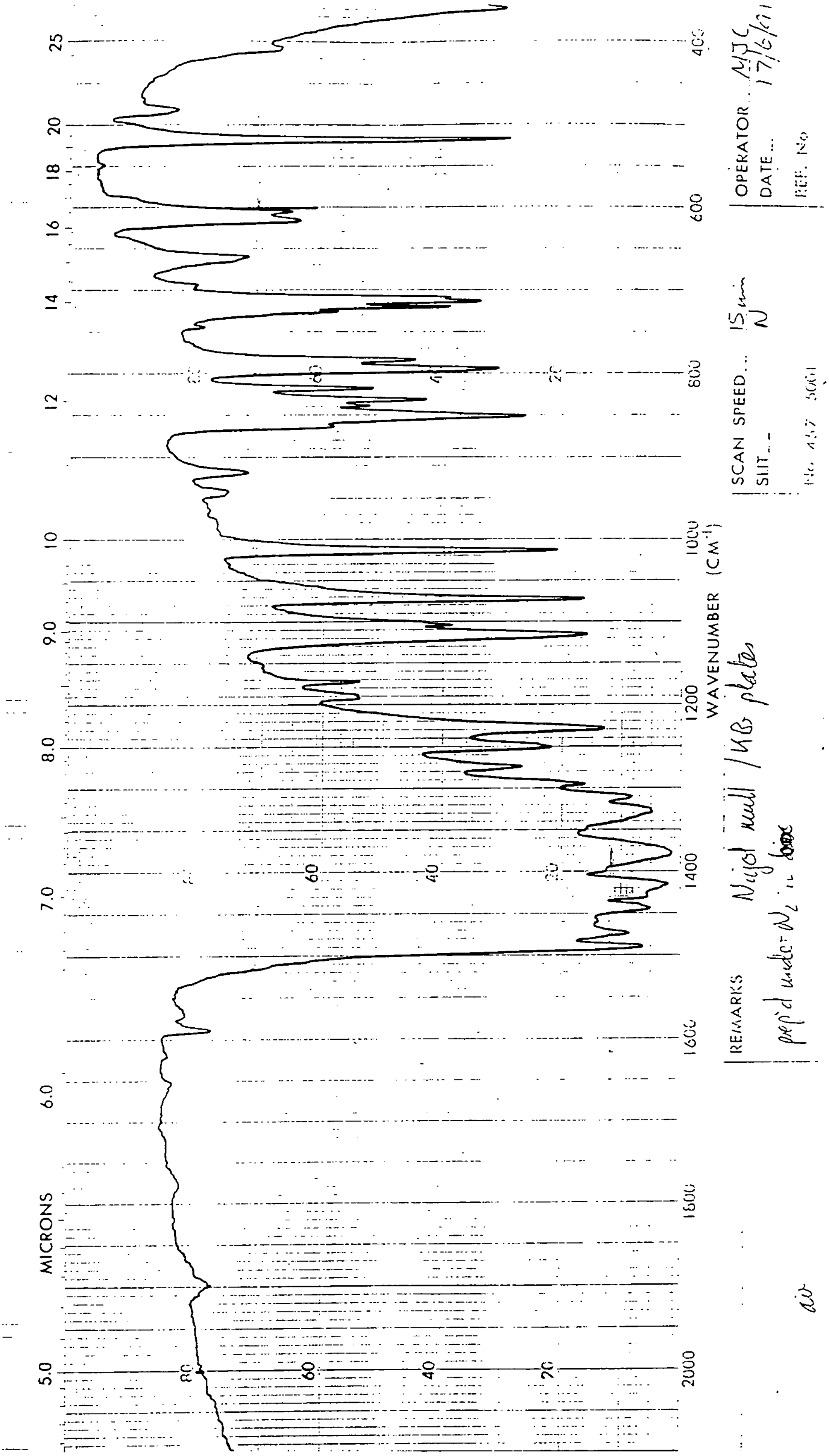
IR spectrum of $(PhNBCl)_3$



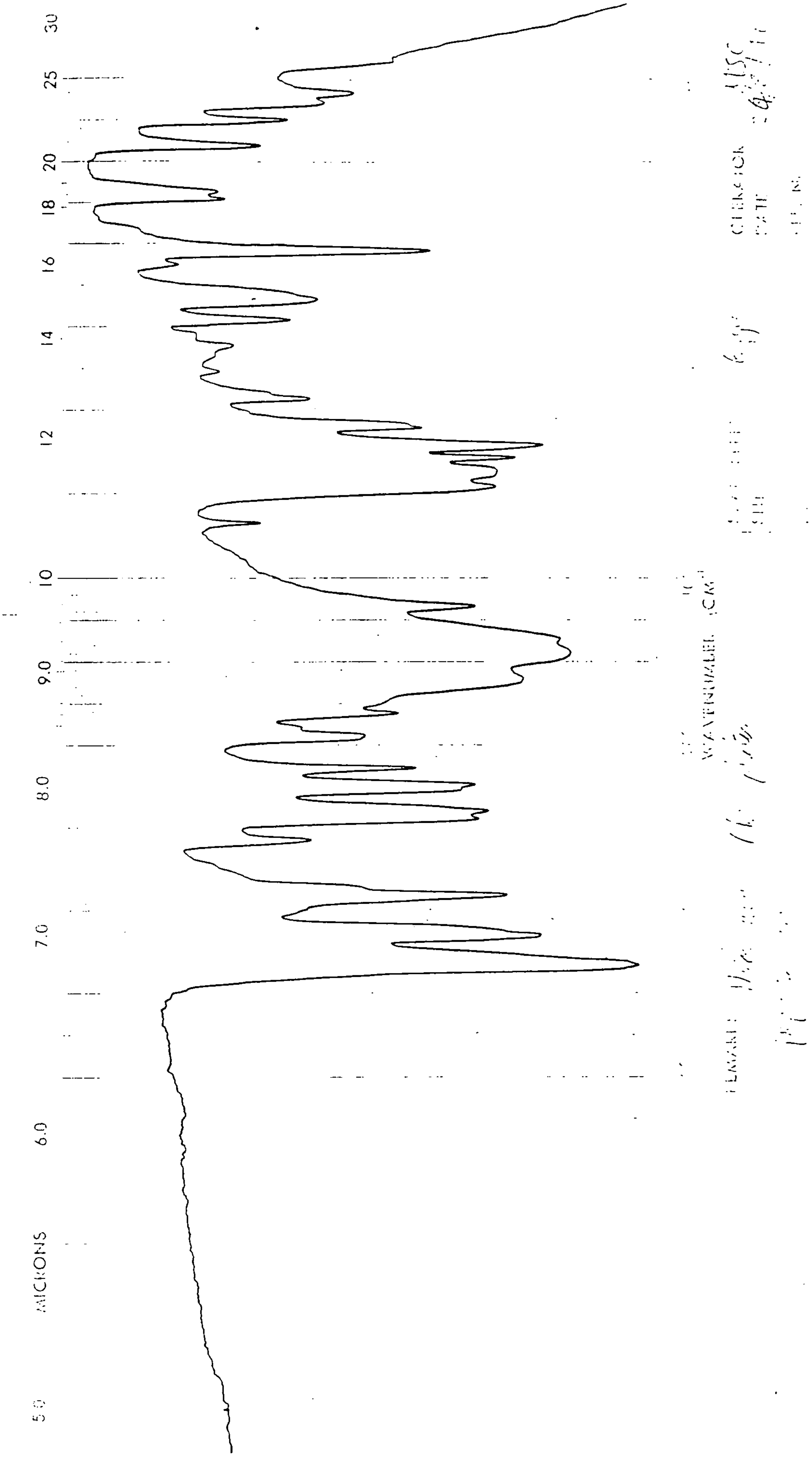
IR spectrum of $(pBrC_6H_4NBCl)_3$



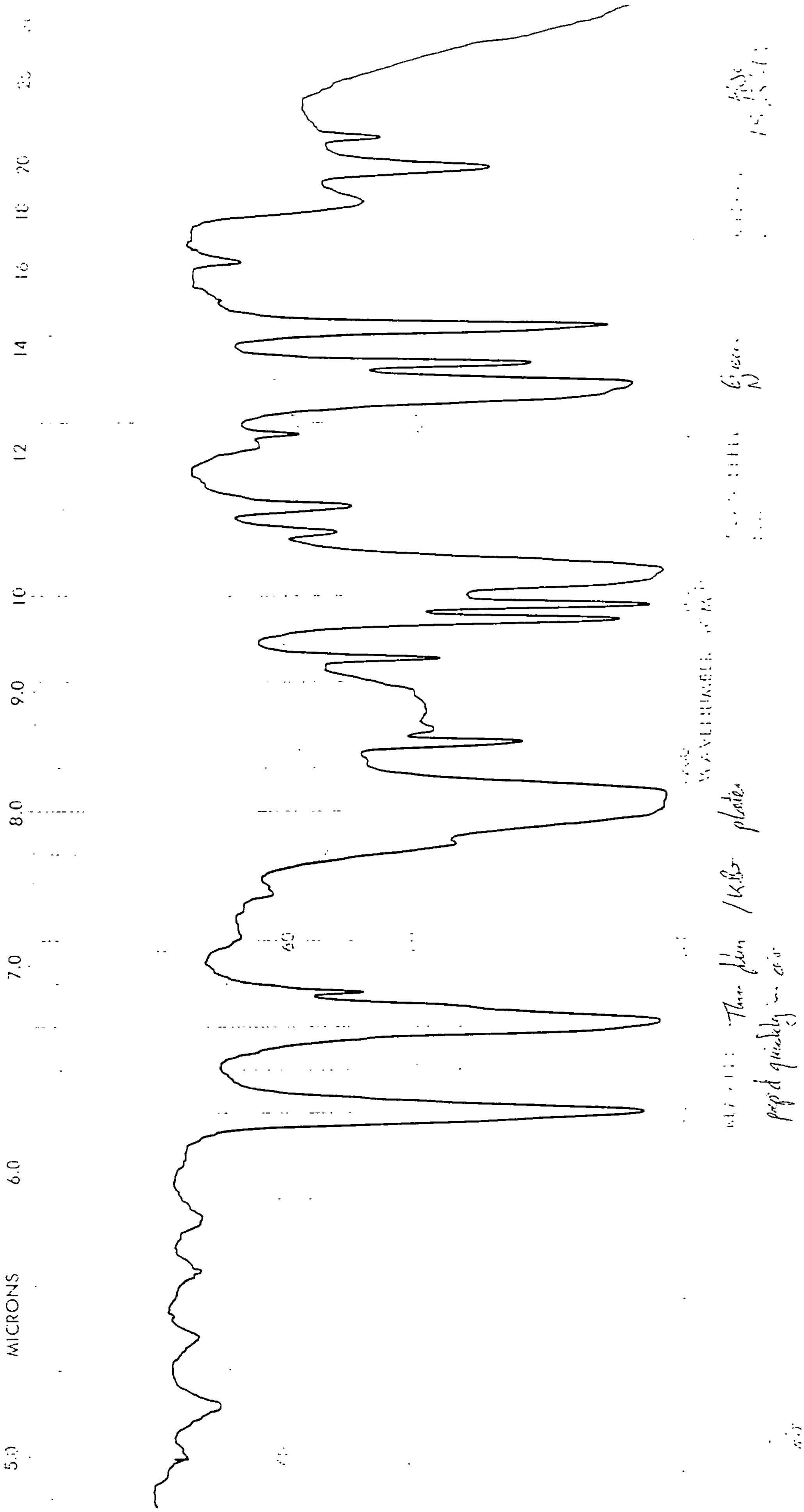
IR spectrum of (PhNBOTBN)3



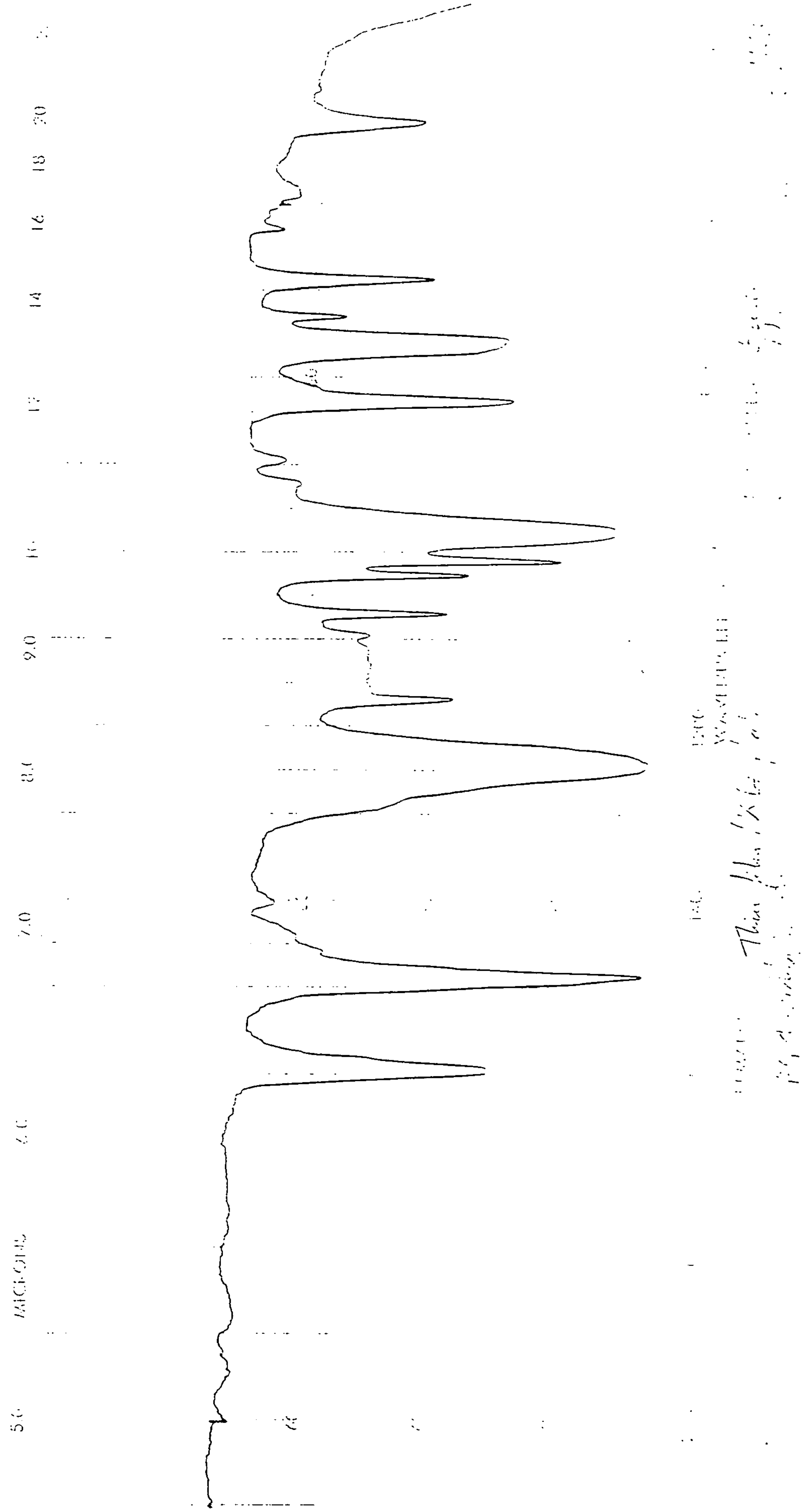
IR spectrum of $(pBrC_6H_4NBOTBN)_3$



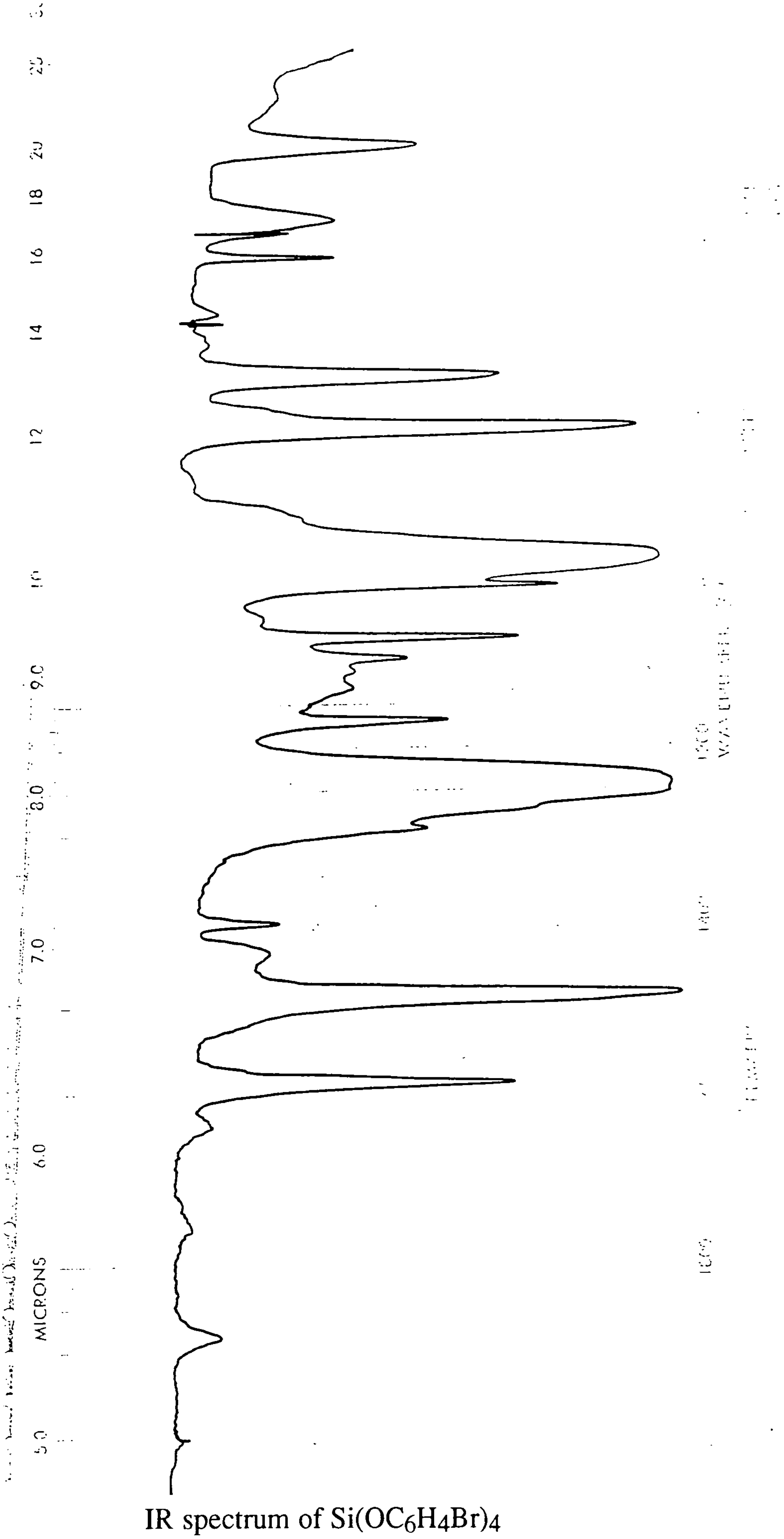
IR spectrum of Si(OTBN)$_4$



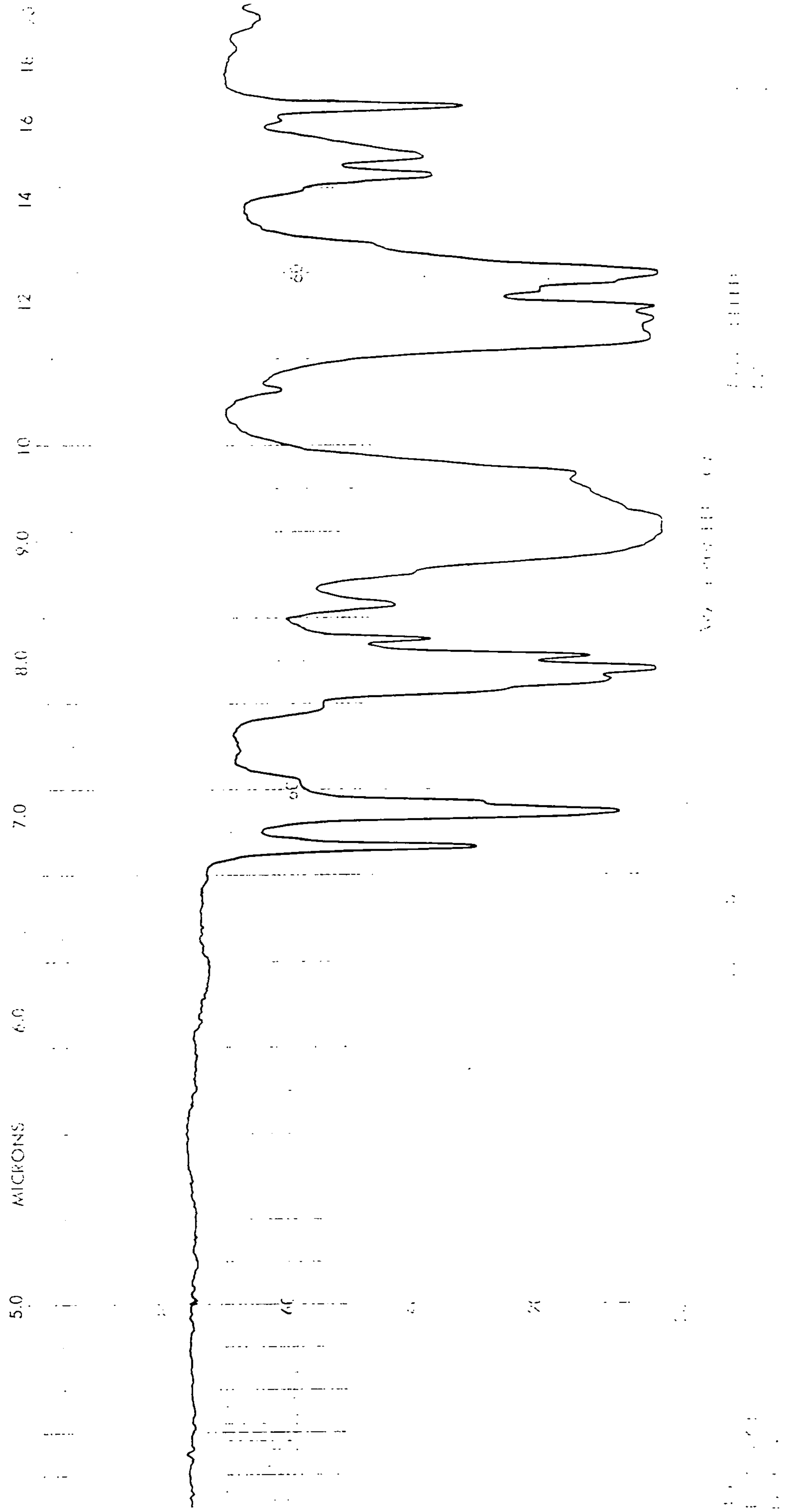
IR spectrum of $Si(OPh)_4$



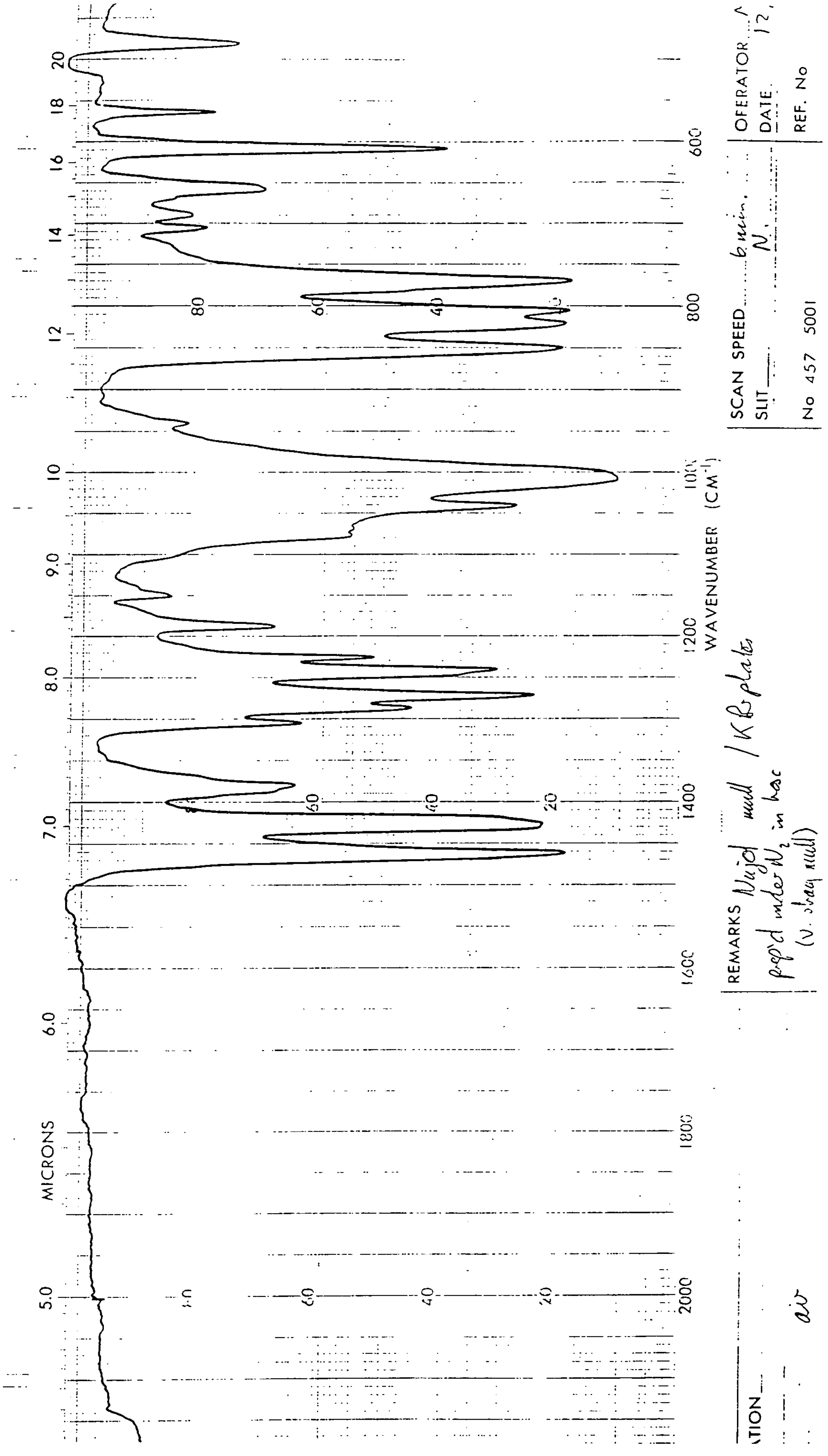
IR spectrum of $(PhO)_2Si(OC_6H_4Br)_2$



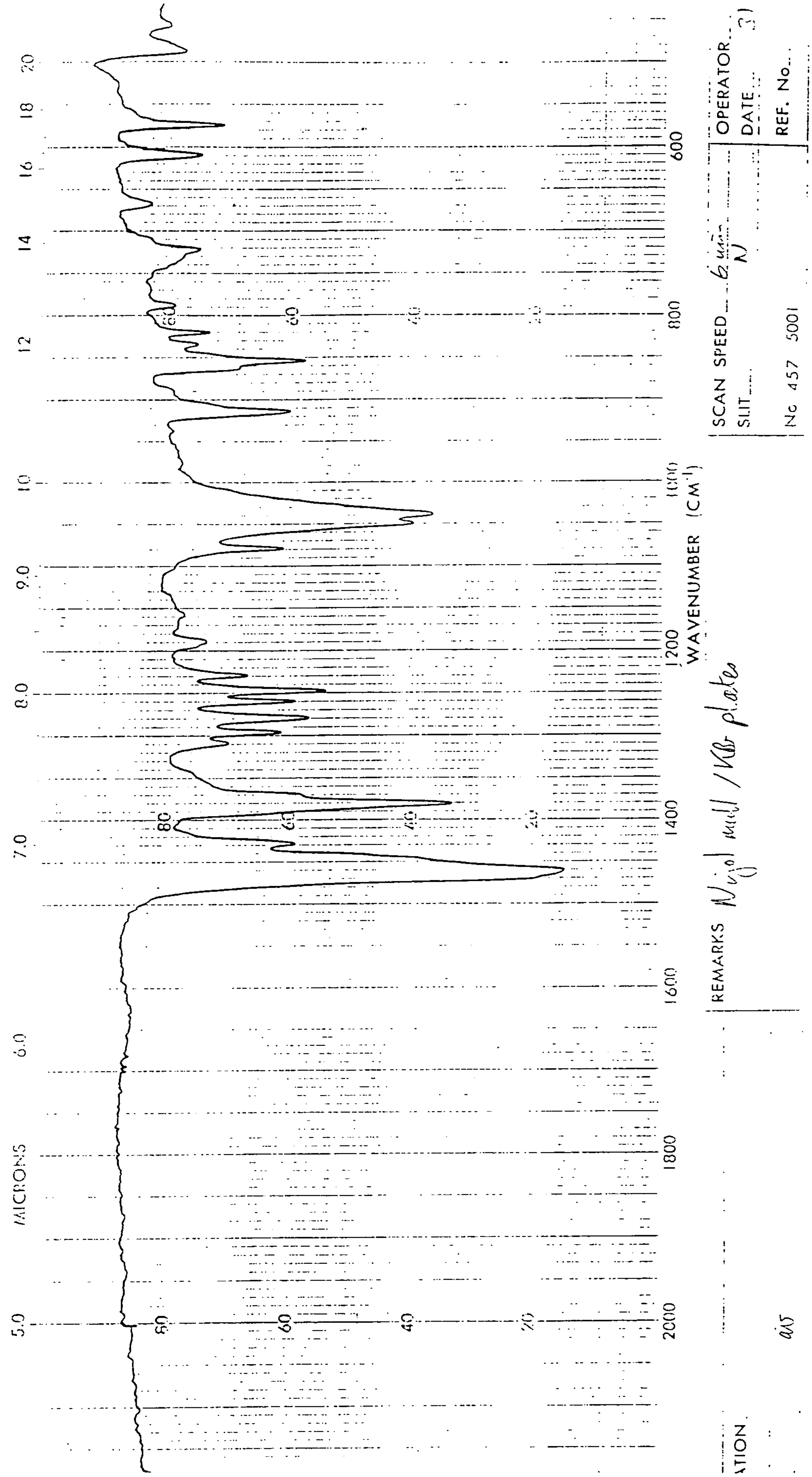
IR spectrum of $Si(OC_6H_4Br)_4$



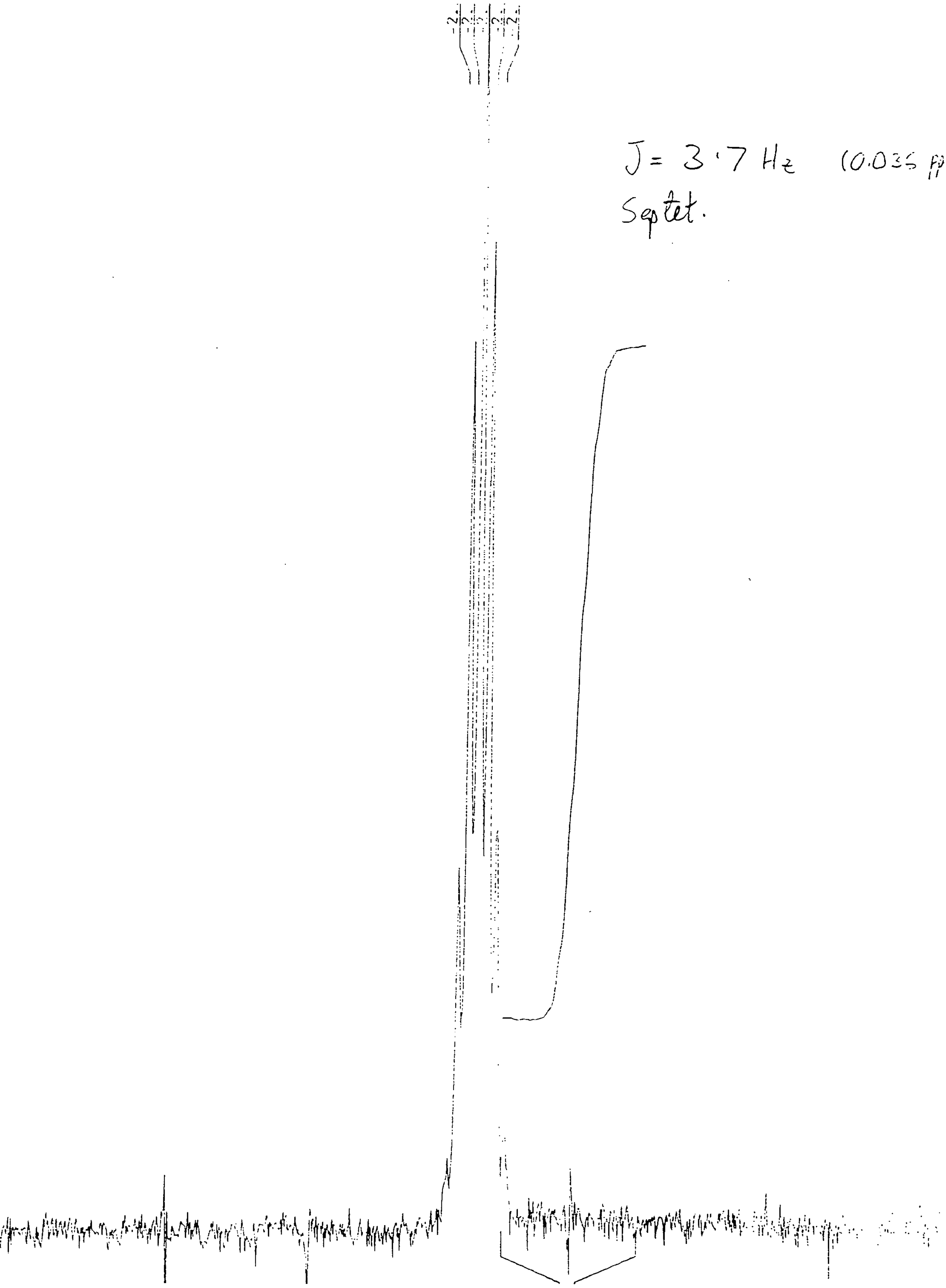
IR spectrum of $Me_2Si(OTBN)_2$



IR spectrum of P(OTBN)3



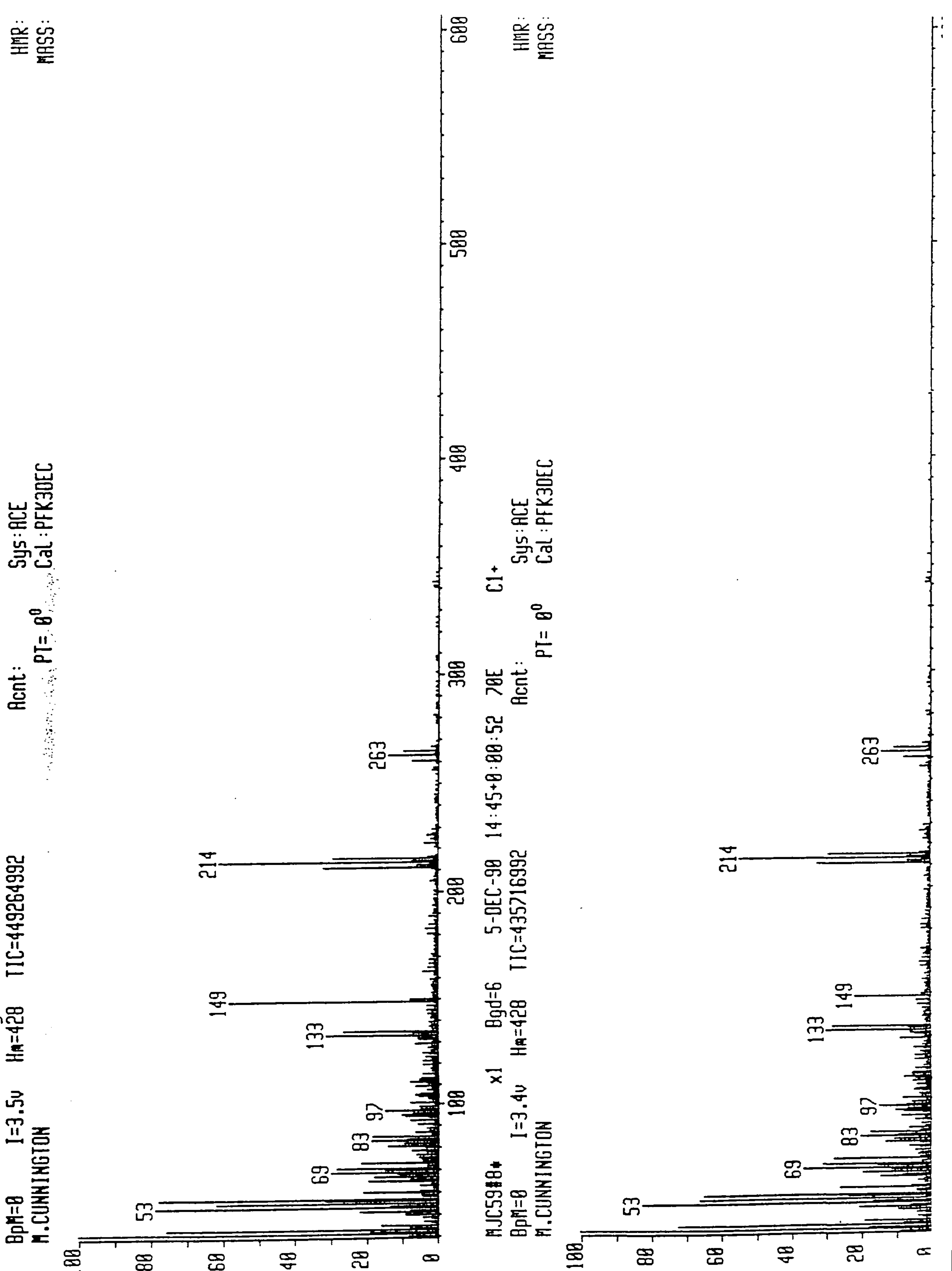
IR spectrum of P(O)(OTBN)$_3$



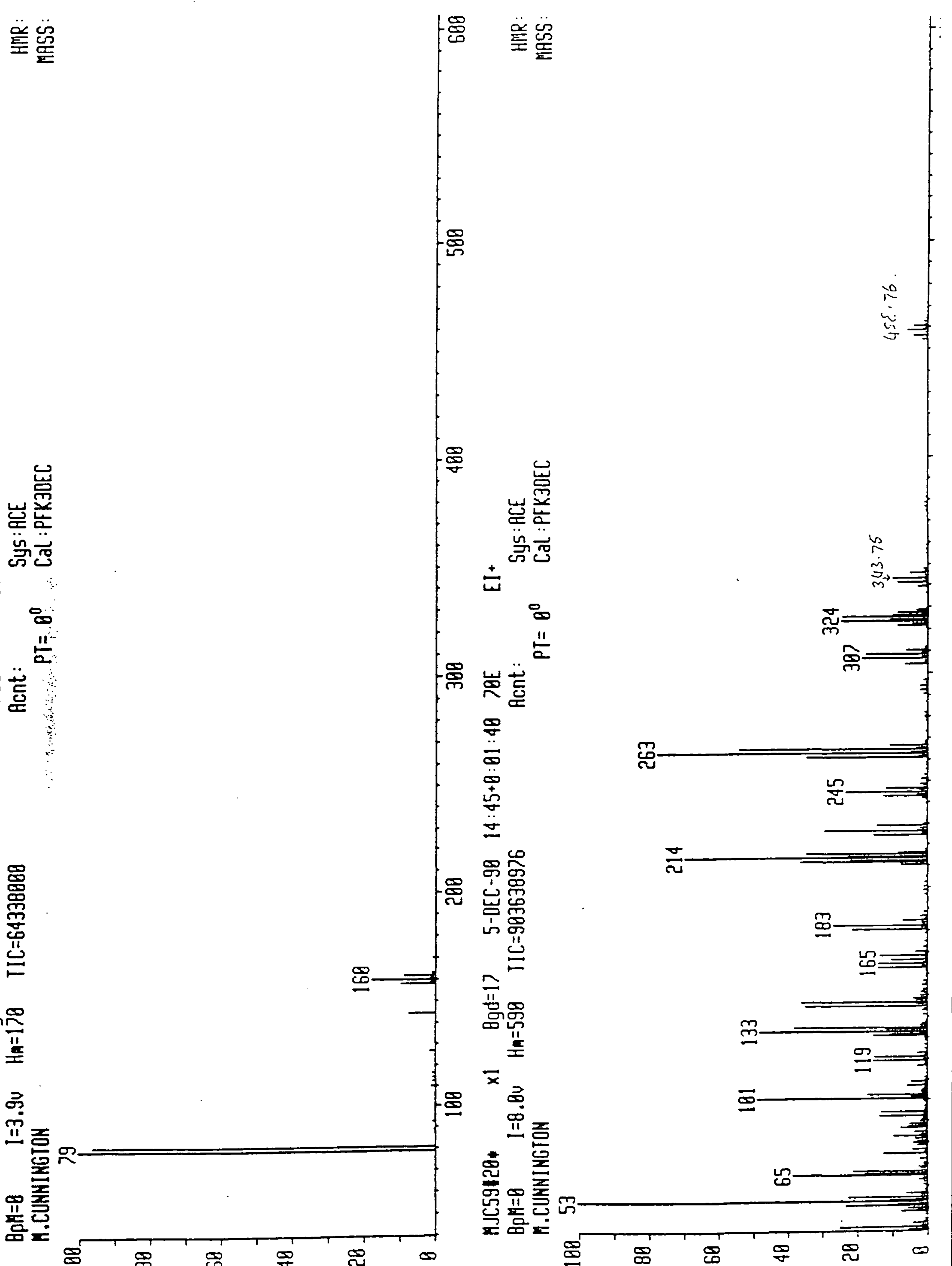
J= 3·7 Hz (0.035 pp

Septet.

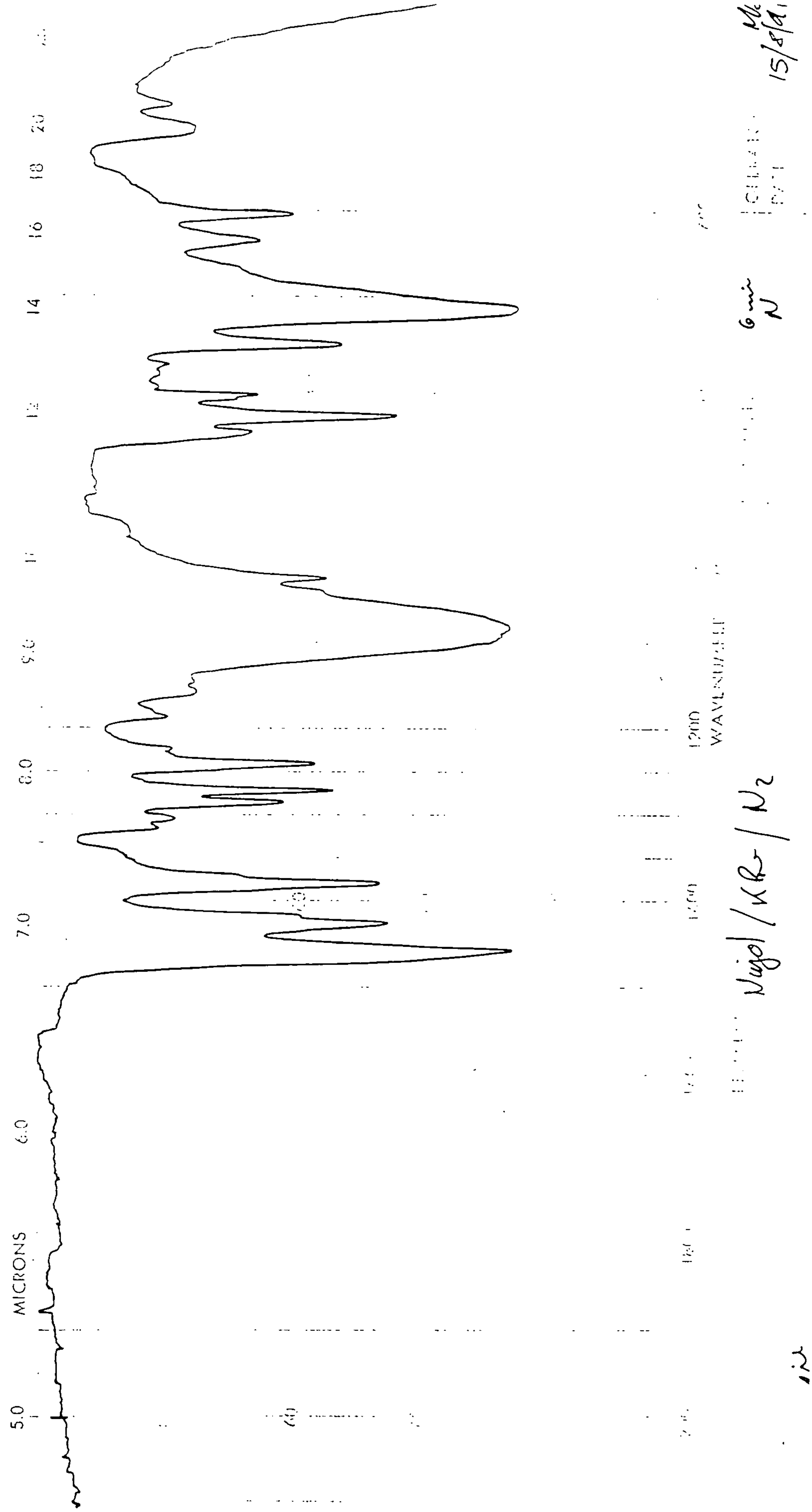
^{31}P NMR spectrum of P(O)(OTBN)$_3$



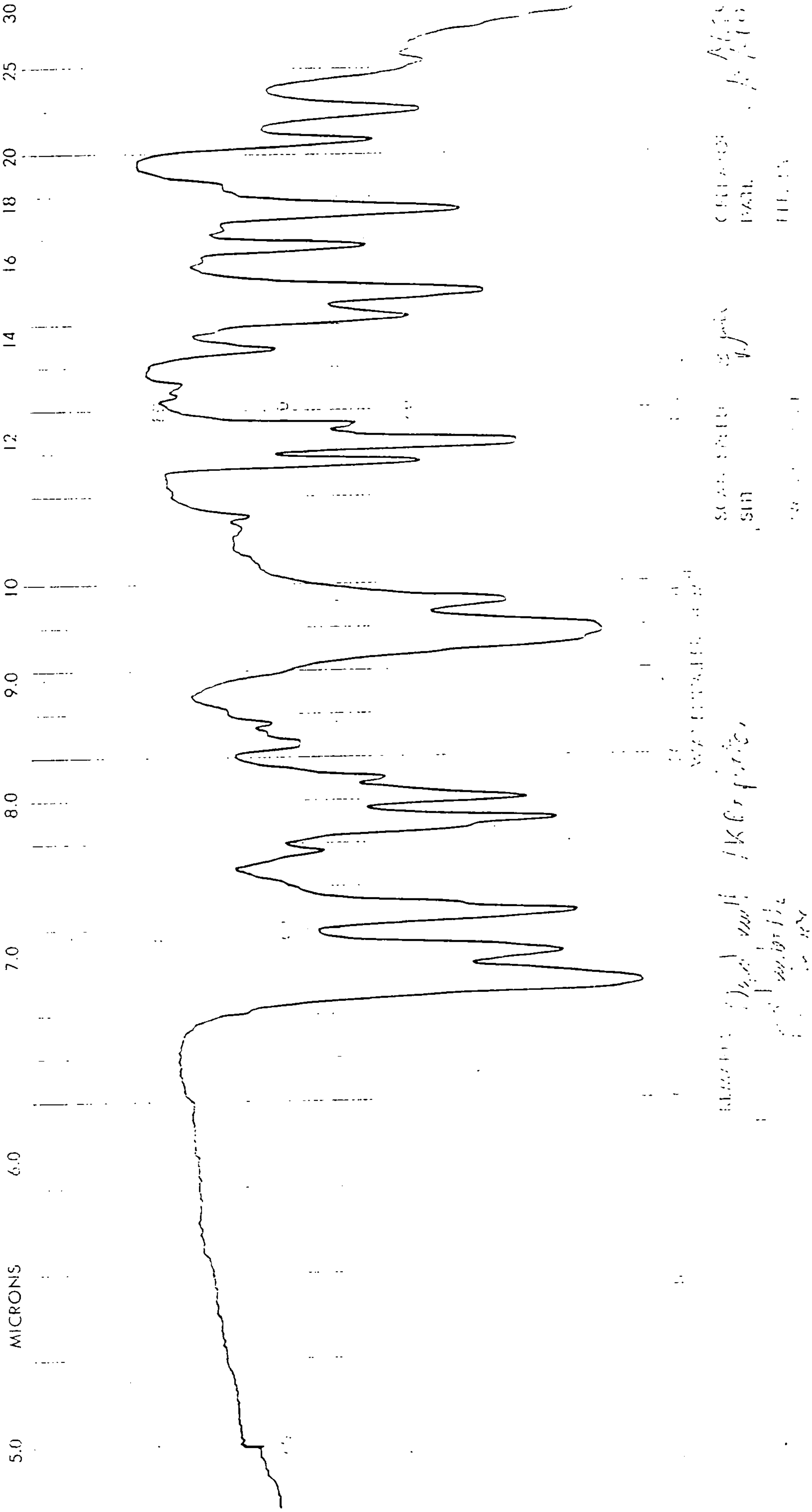
Mass spectrum of P(O)(OTBN)$_3$



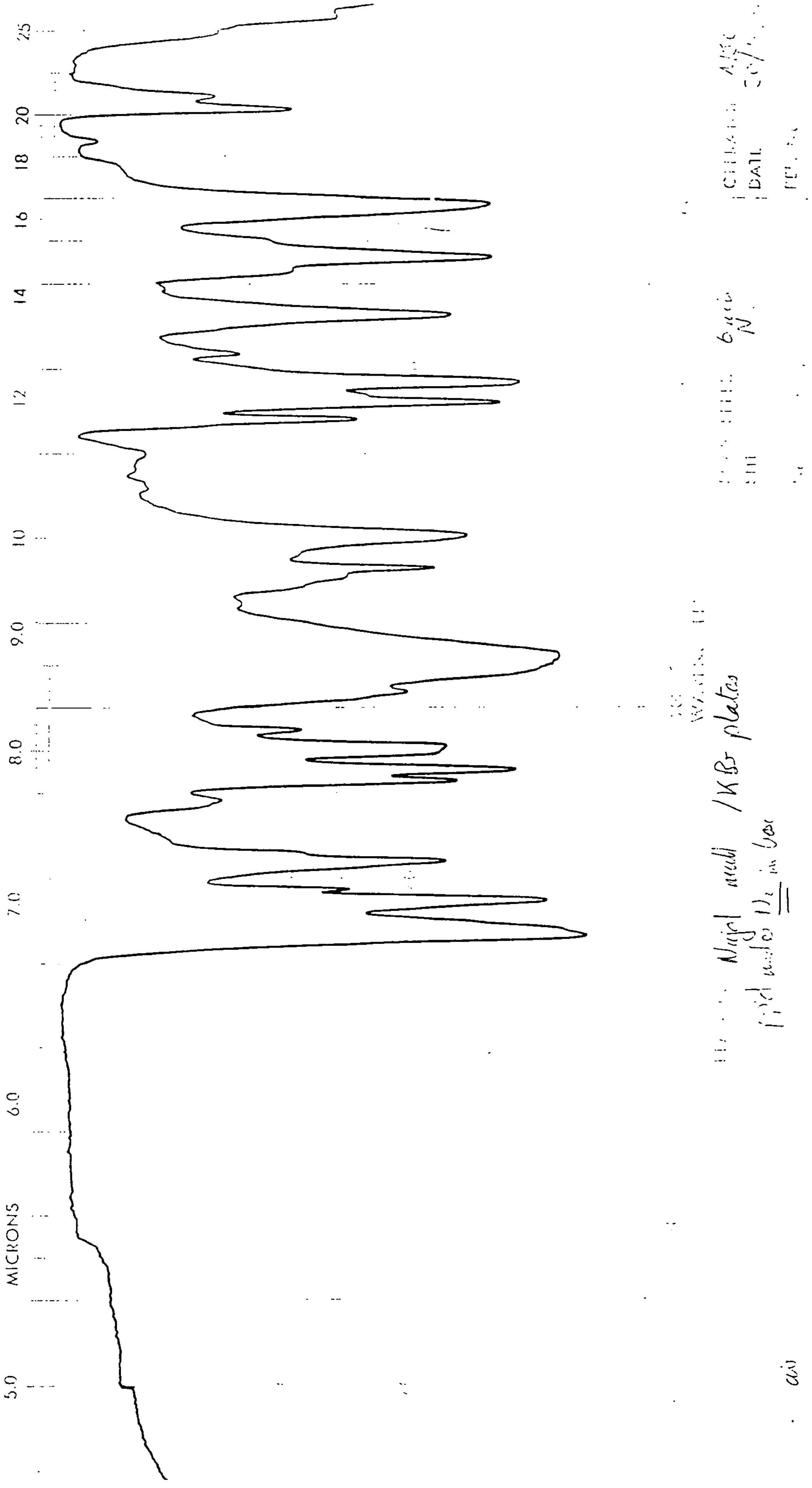
Mass spectrum of $P(O)(OTBN)_3$



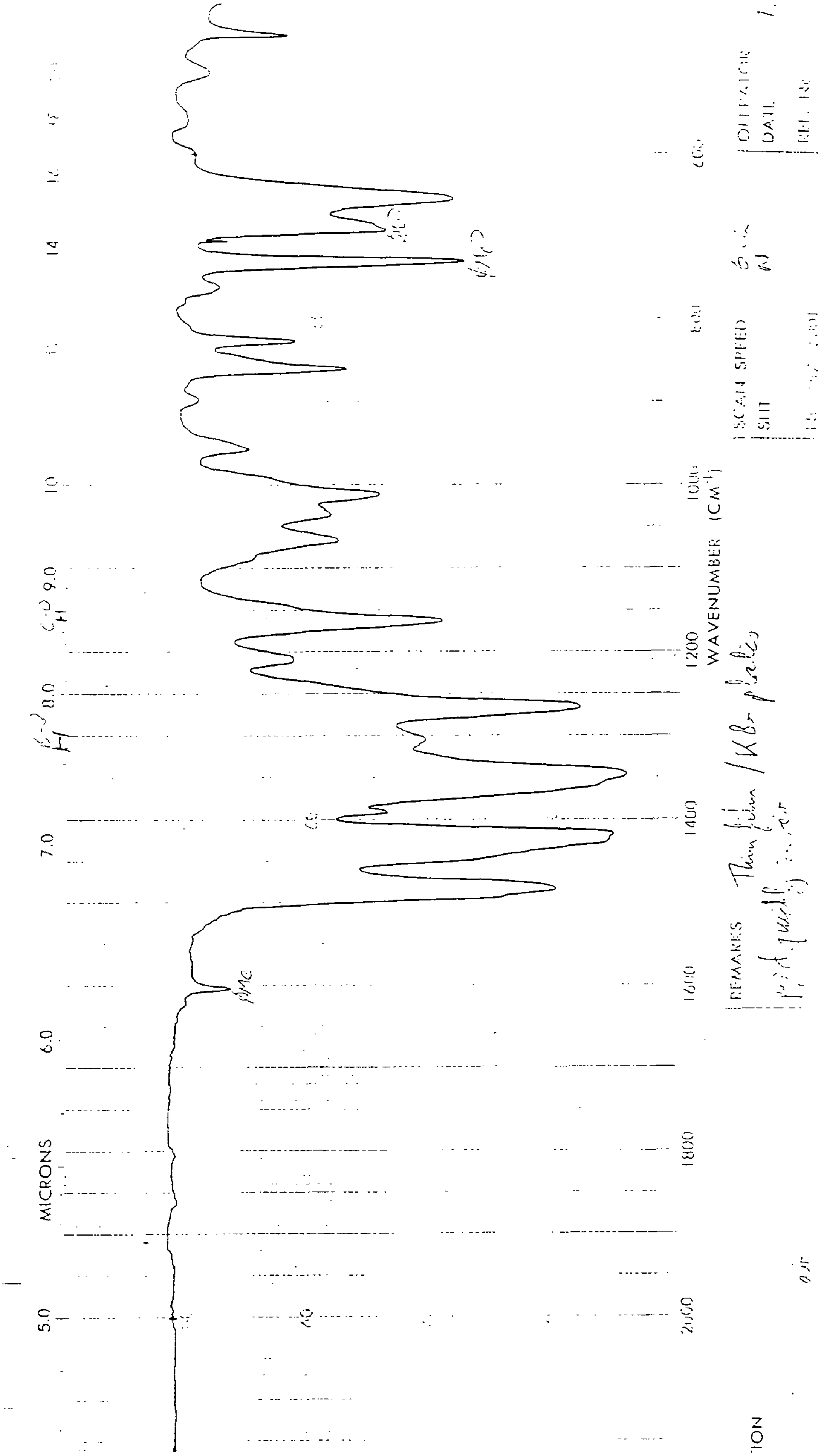
IR spectrum of Ti(OTBN)$_4$



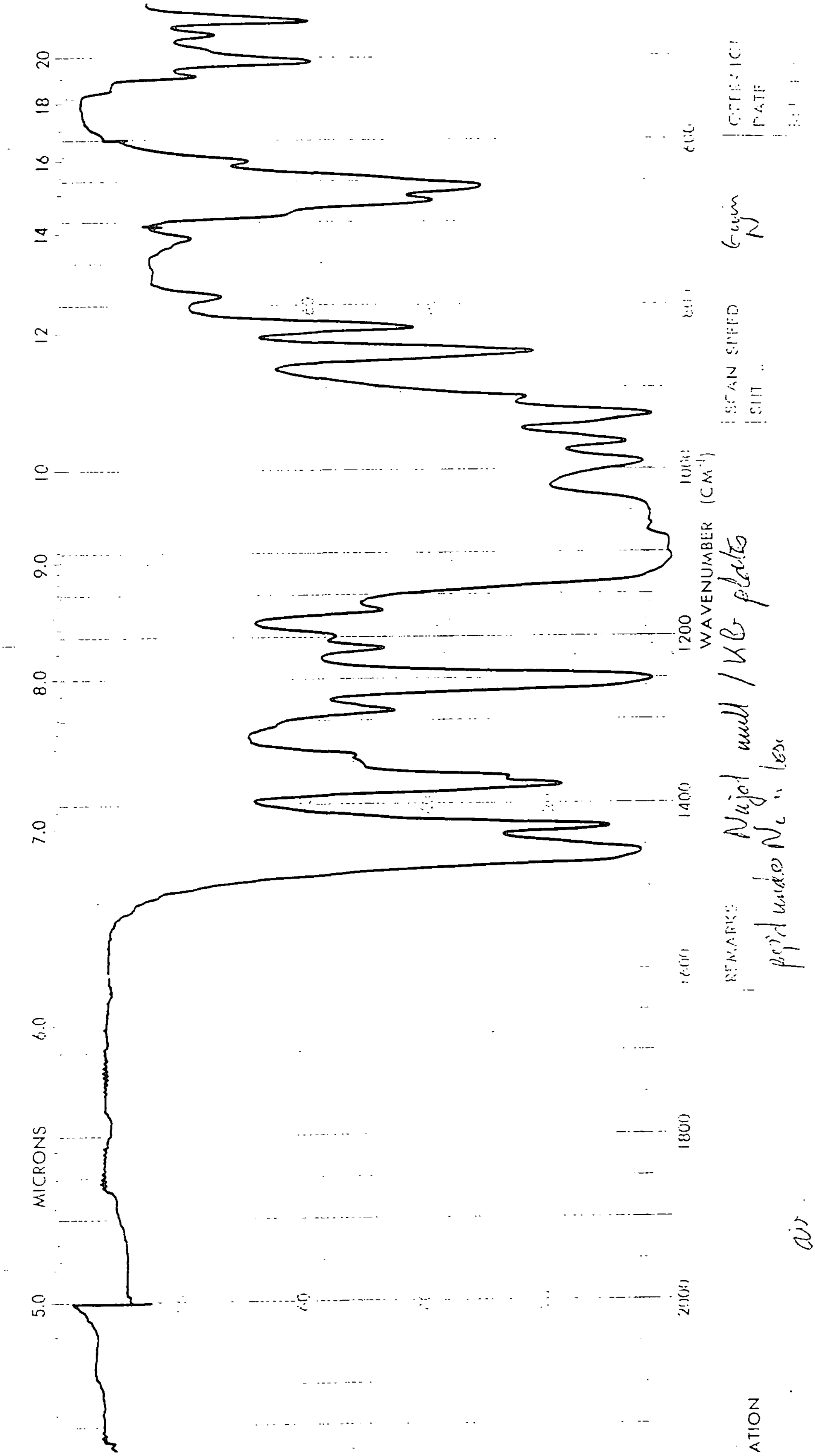
IR spectrum of $Zn(OTBN)_2$



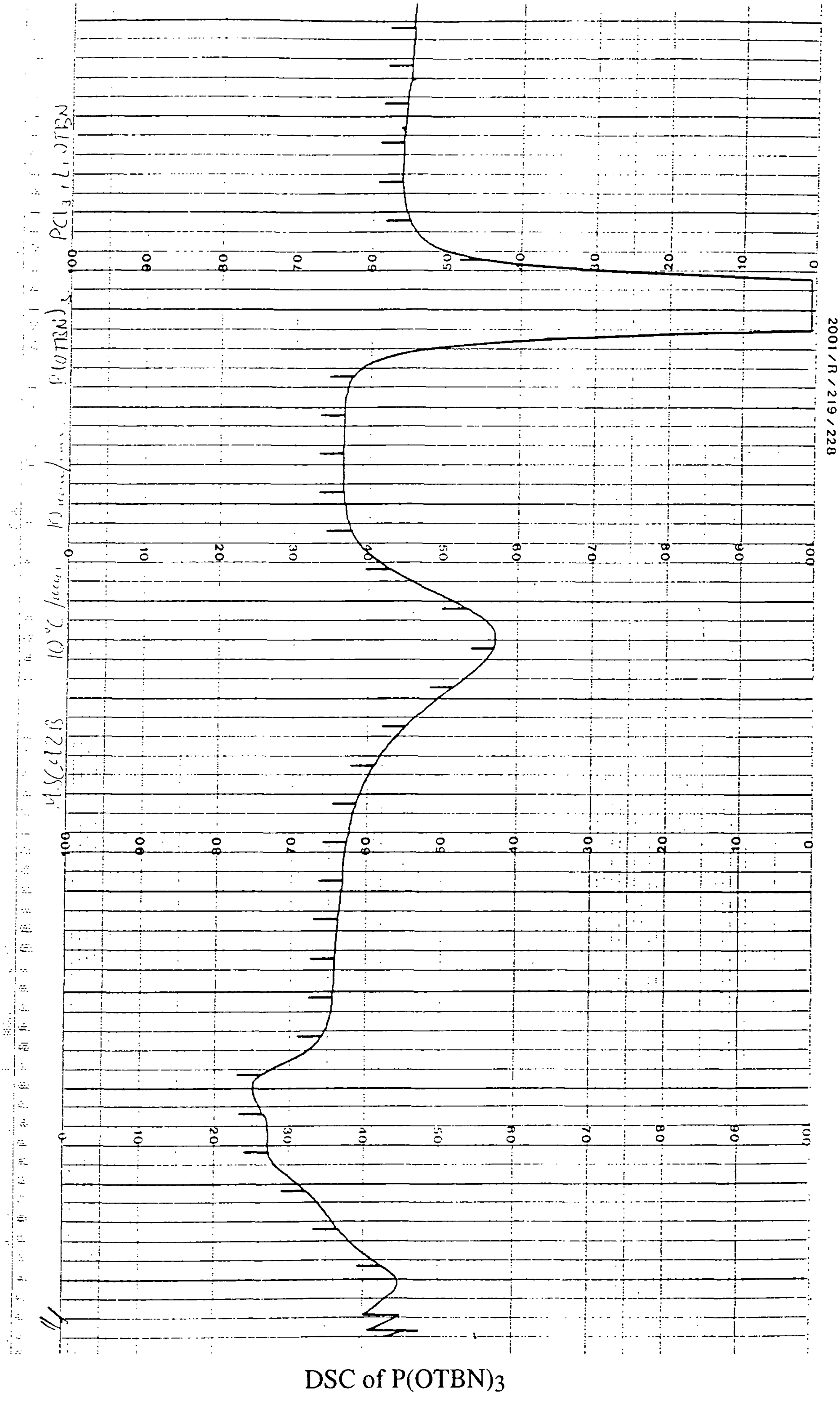
IR spectrum of Al(OTBN)$_3$



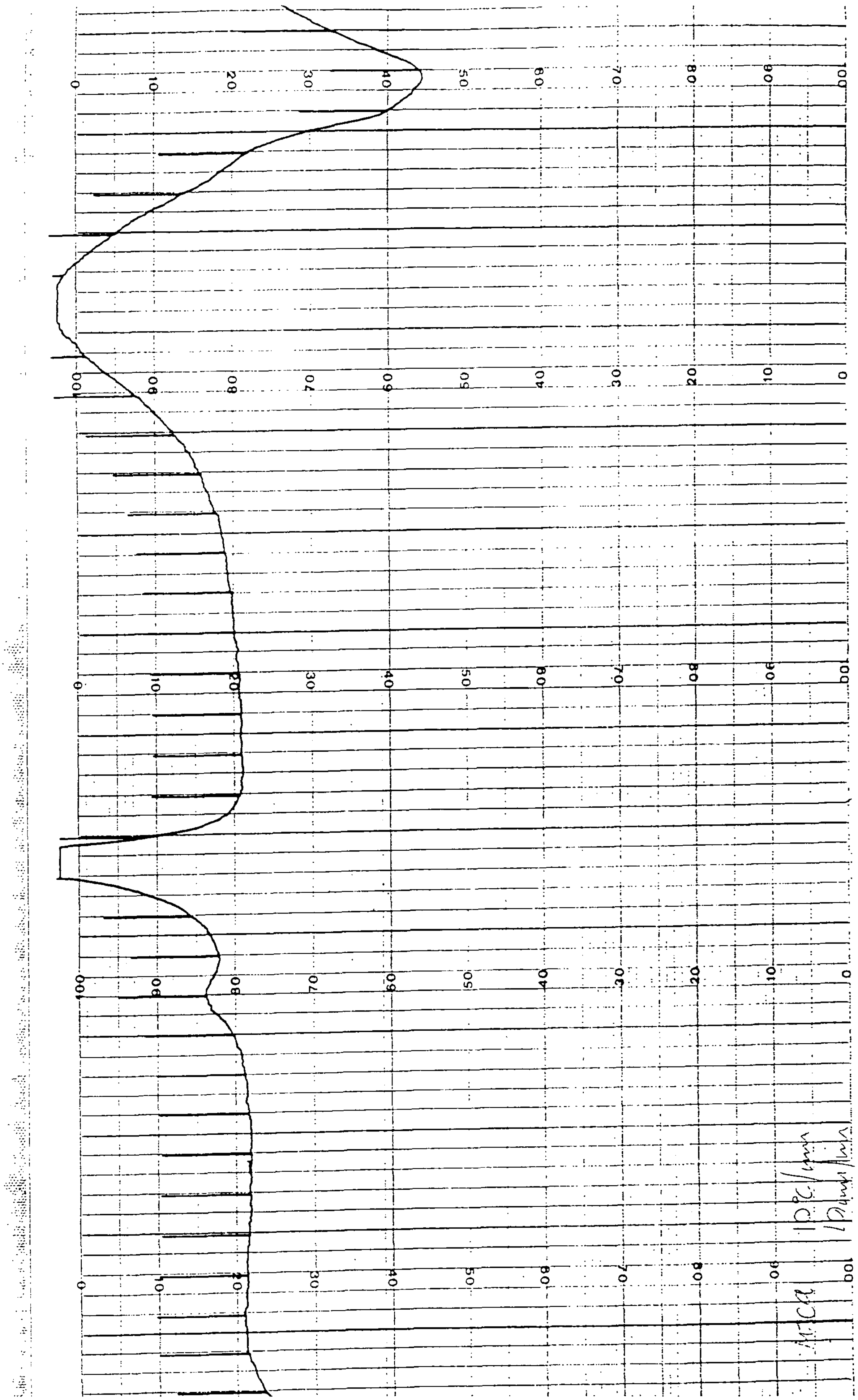
IR spectrum of trisdiol diborate



IR spectrum of NaB(ODBNO)$_2$



DSC of P(OTBN)$_3$



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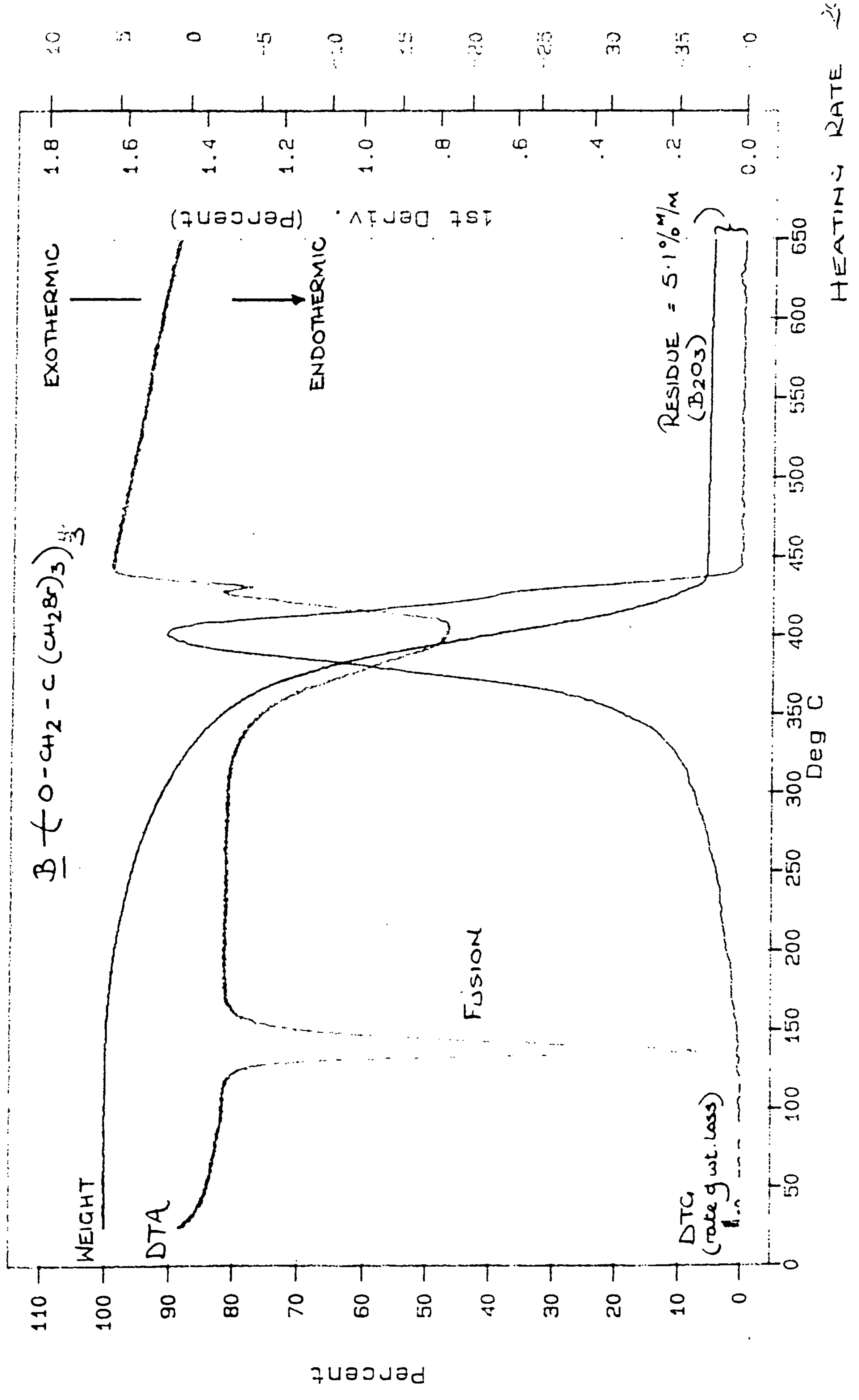
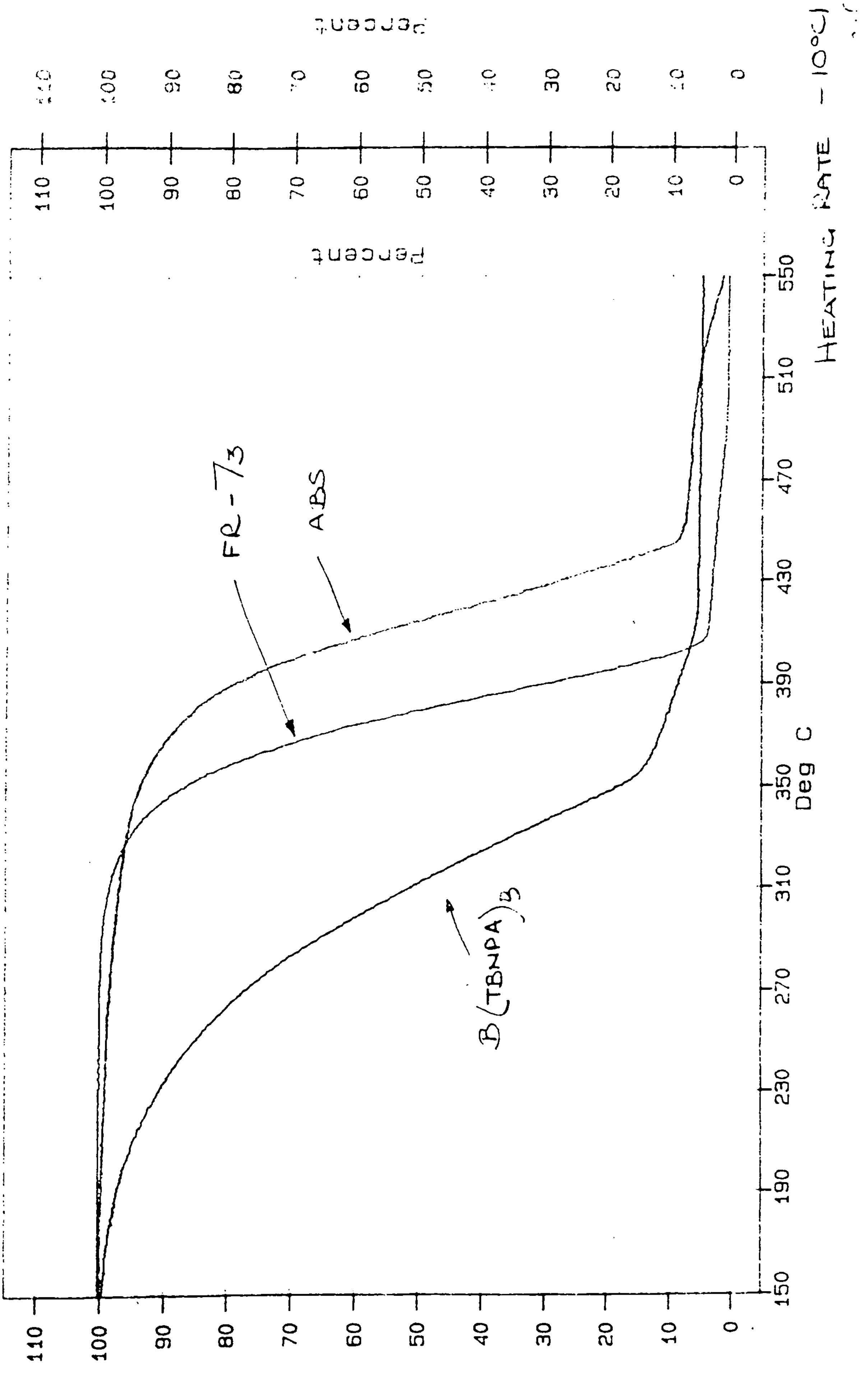
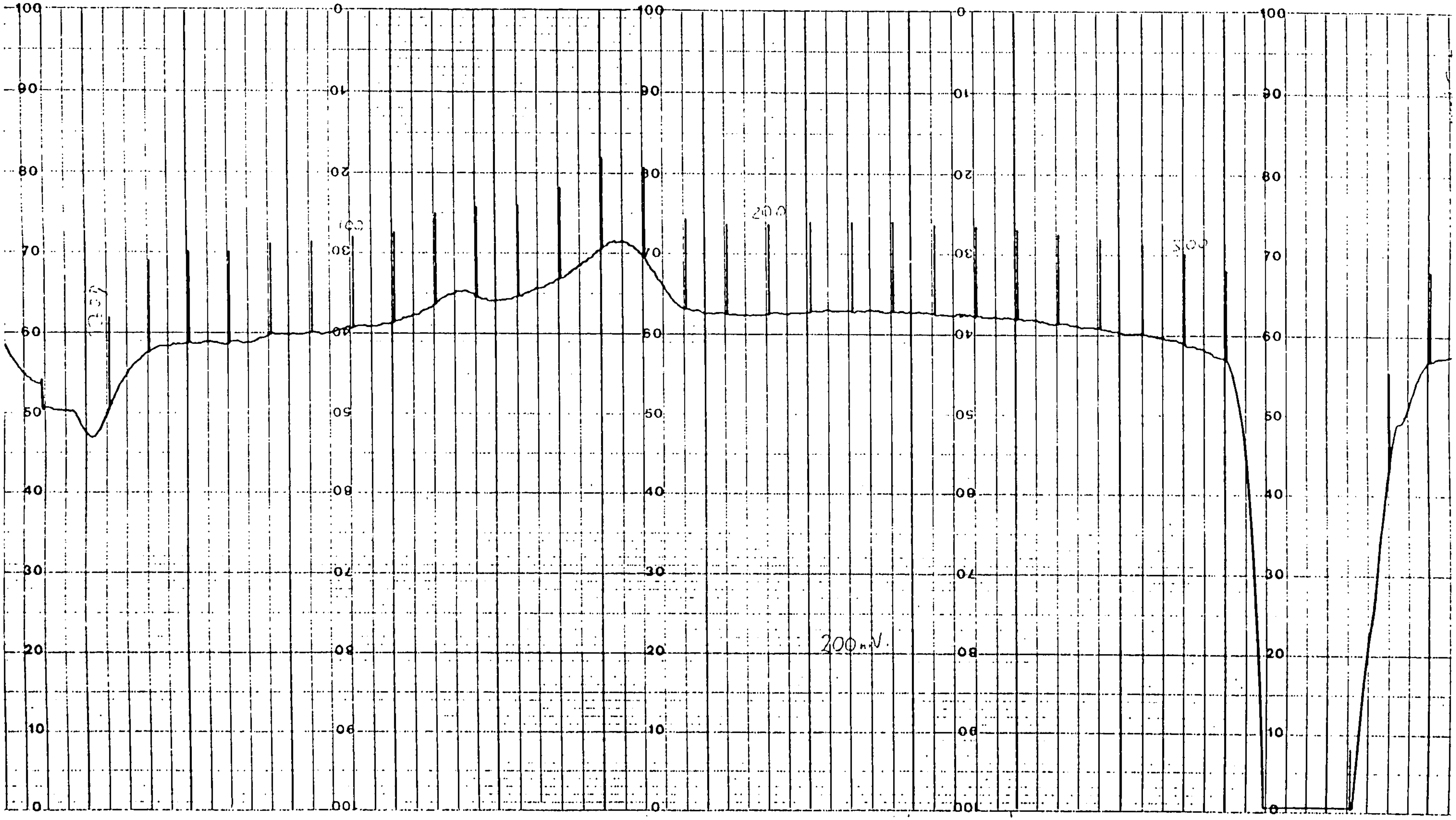


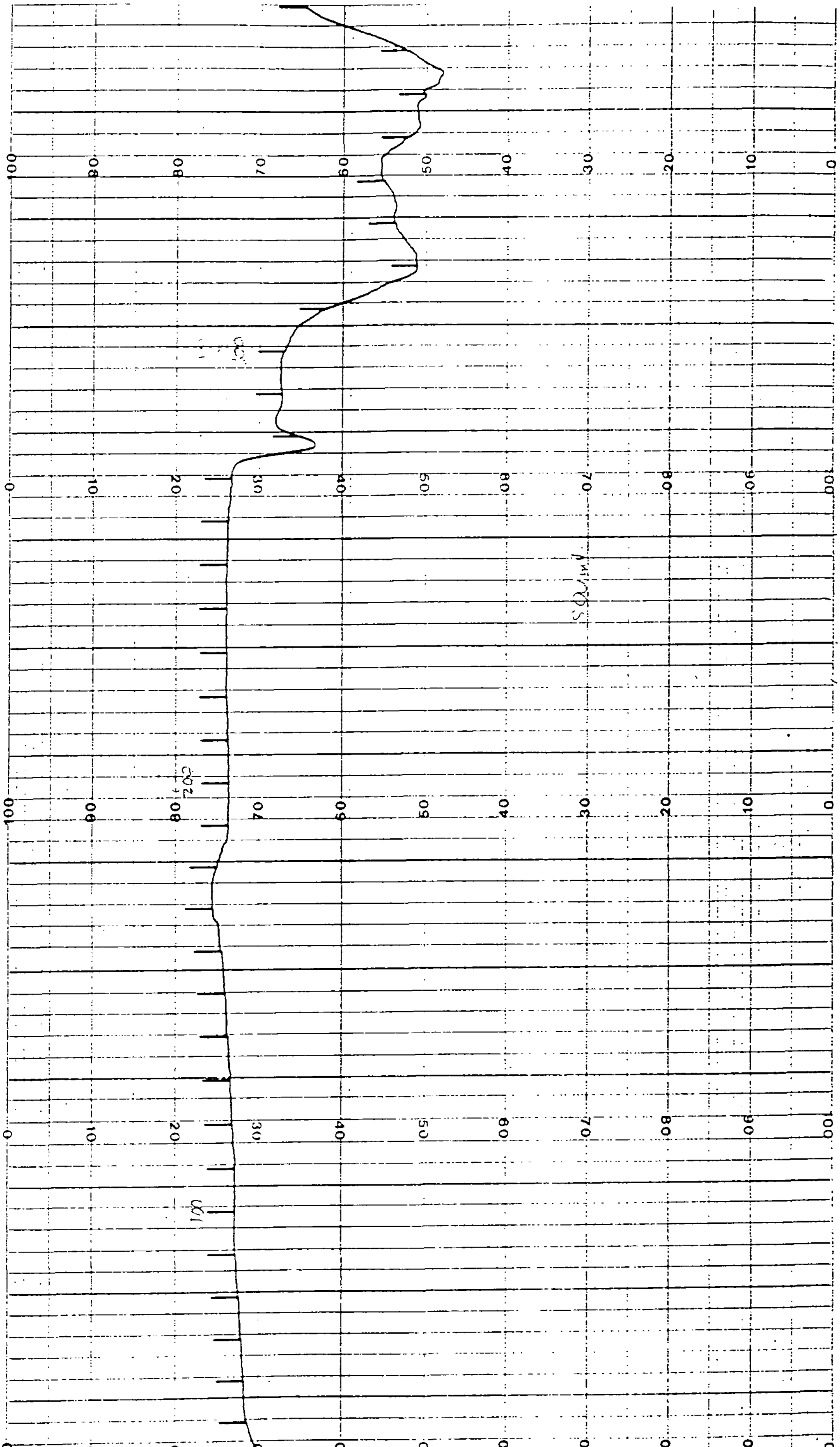
DSC and TGA of B(OTBN)3



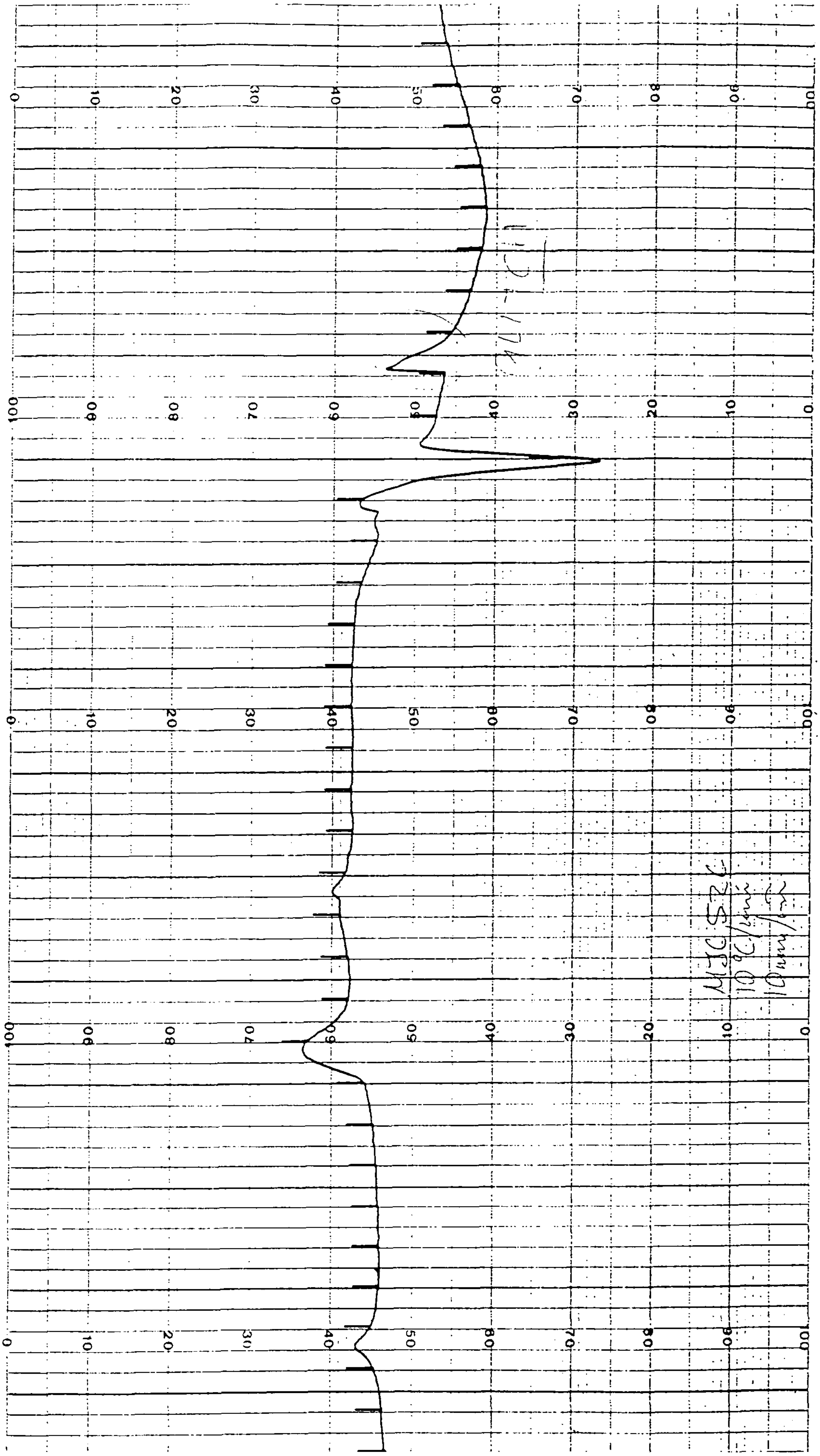
Comparative TGA of B(OTBN)3



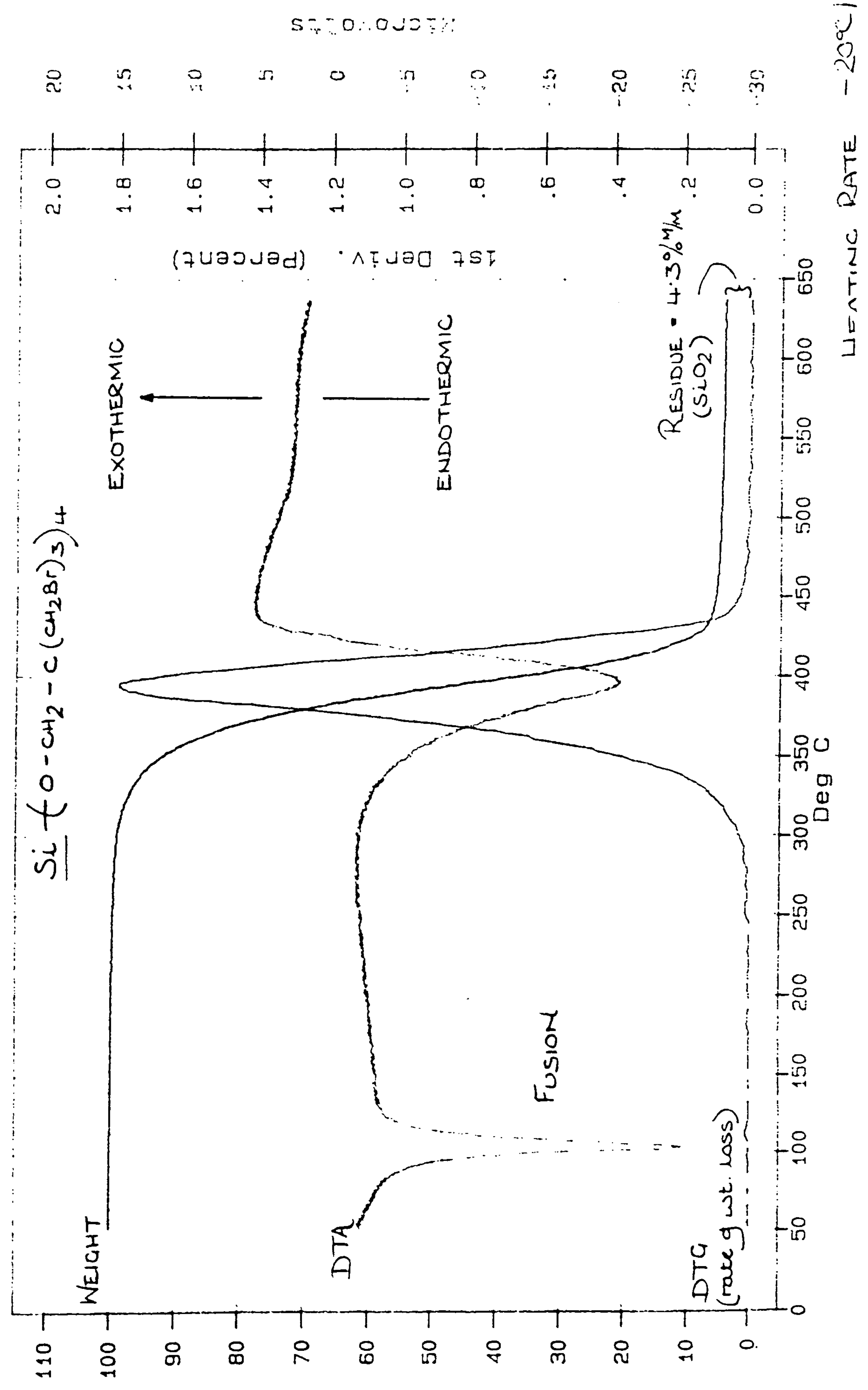
DSC of $(PhNBOTBN)_3$



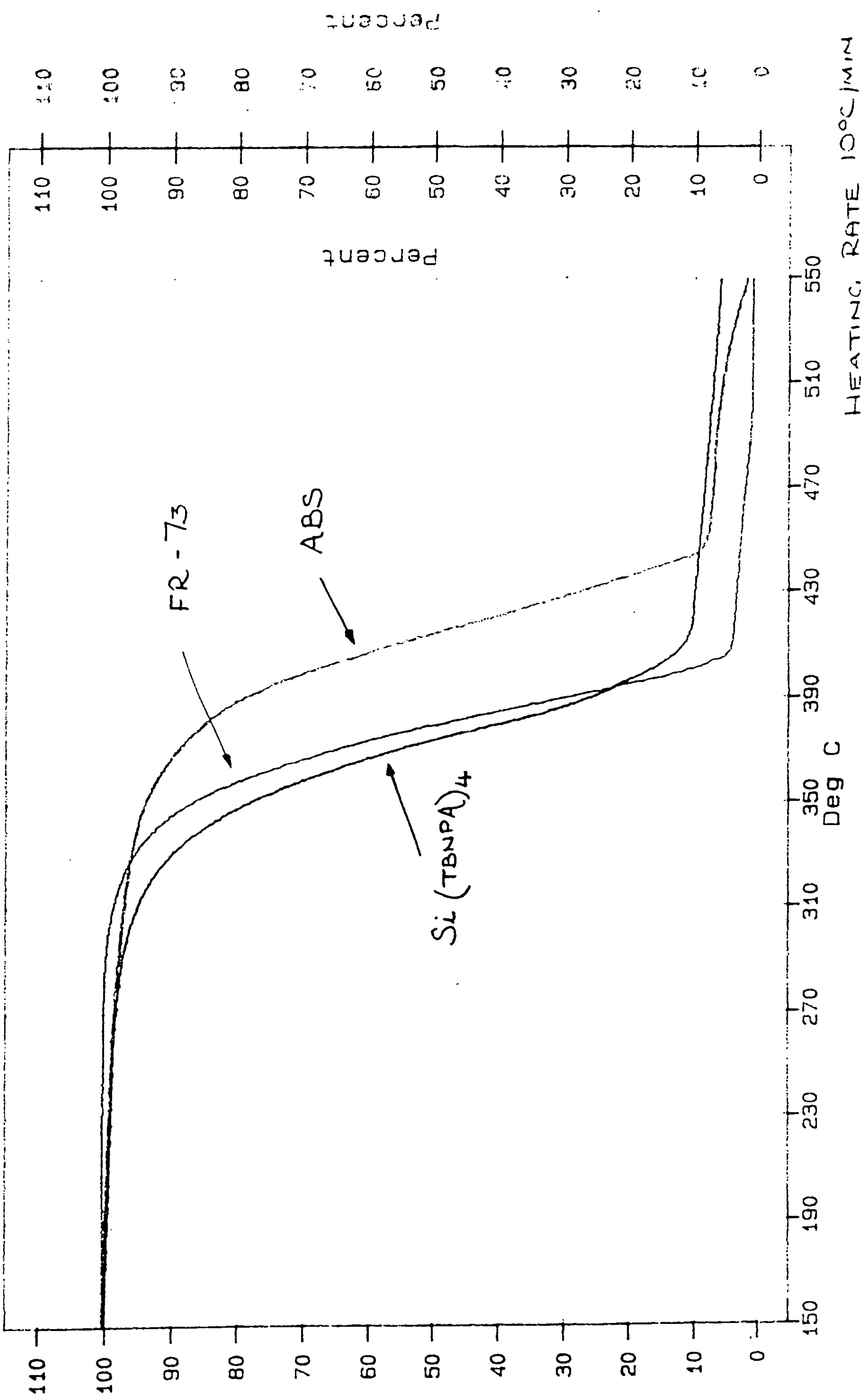
DSC of $(pBrC_6H_4NBOTBN)_3$



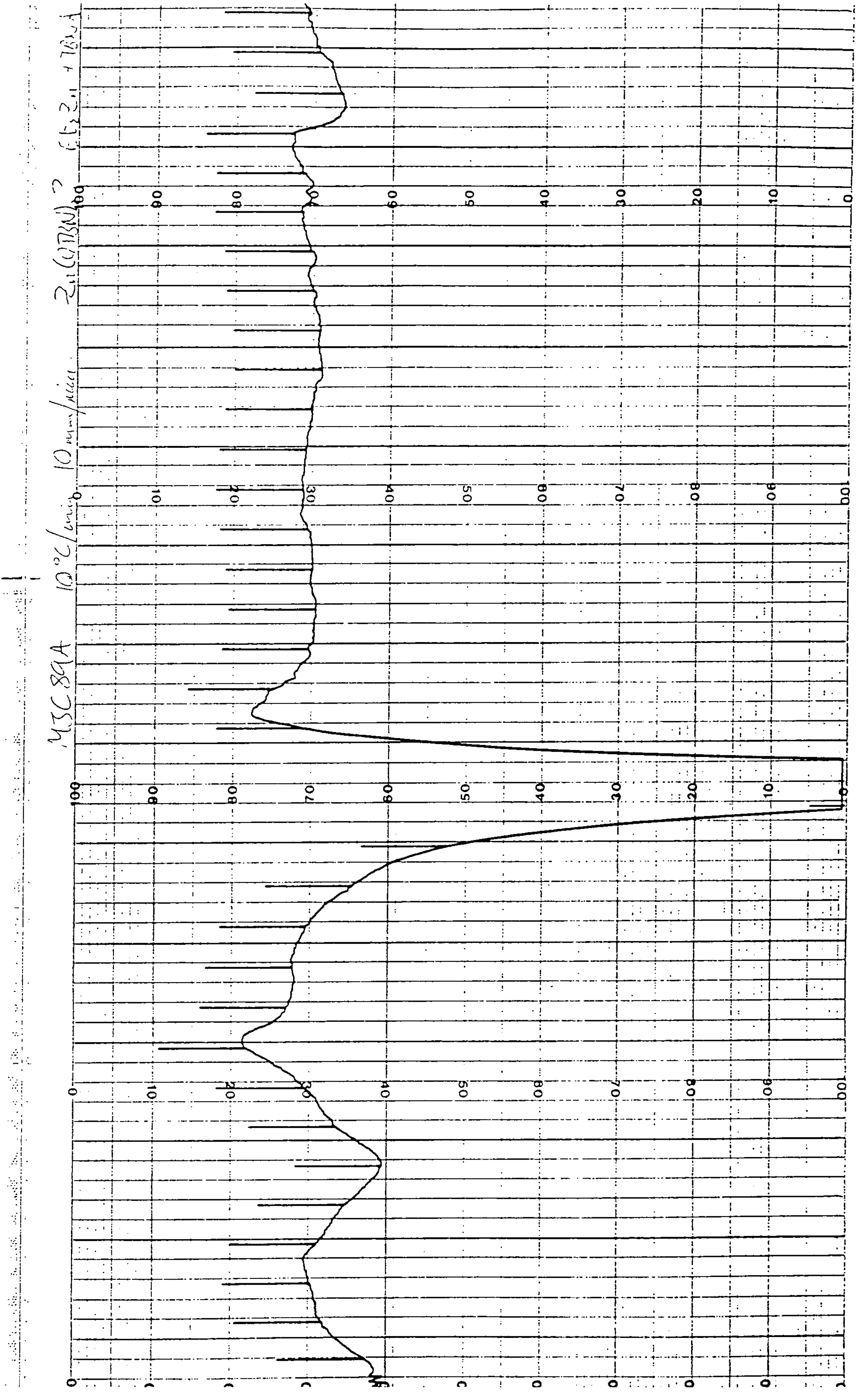
DSC of Al(OTBN)$_3$



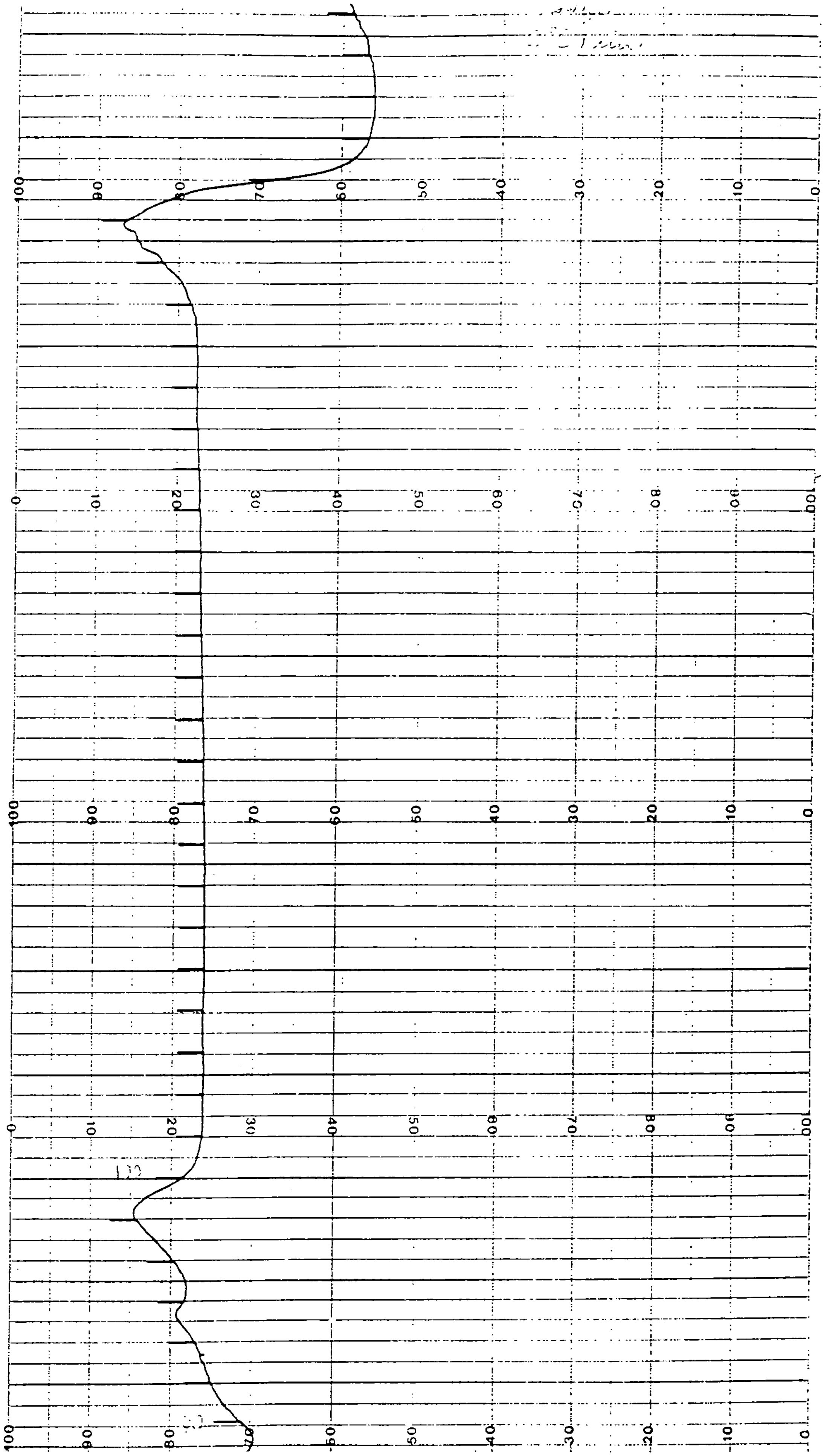
DSC and TGA of $Si(OTBN)_4$



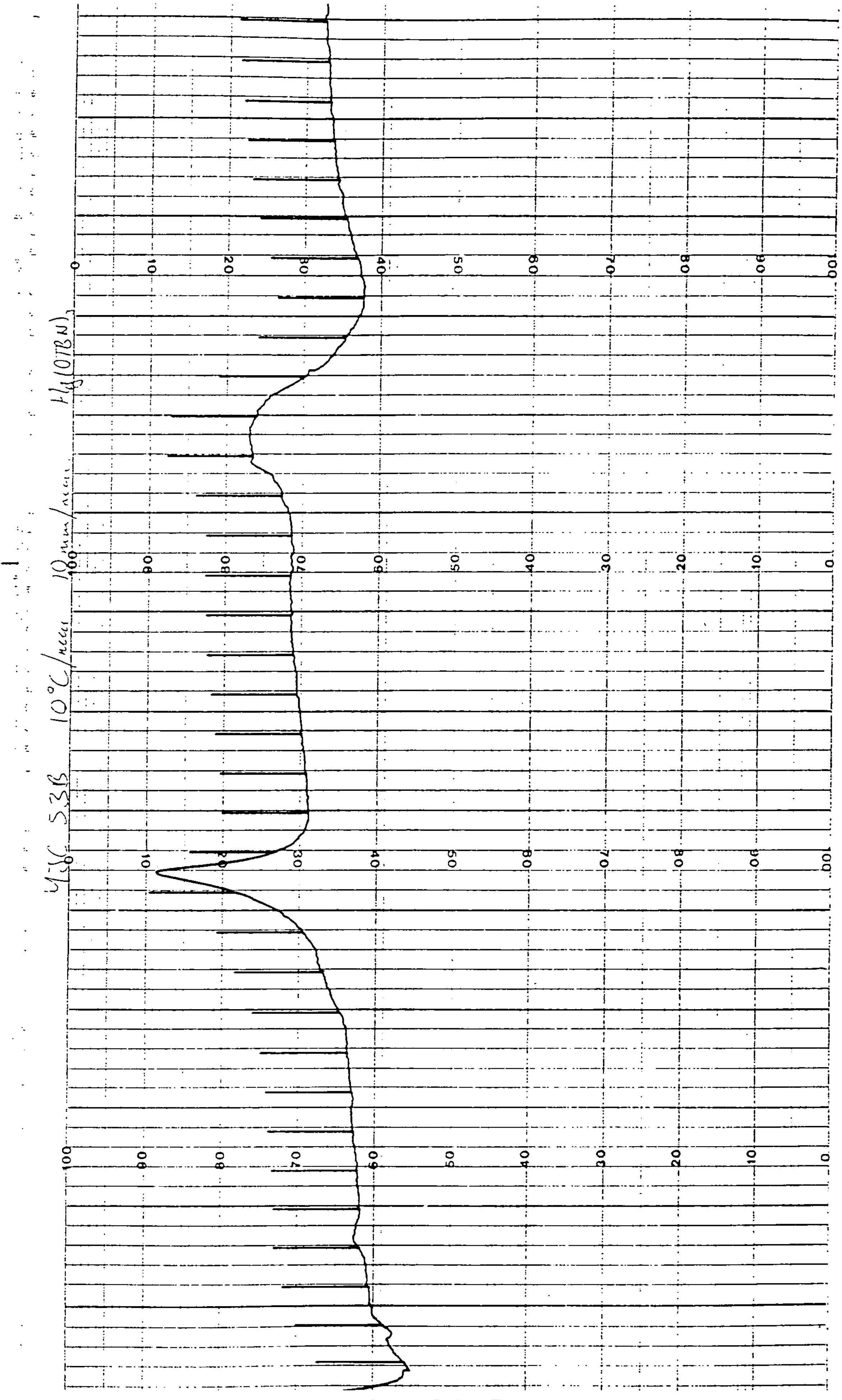
Comparative TGA of Si(OTBN)$_4$



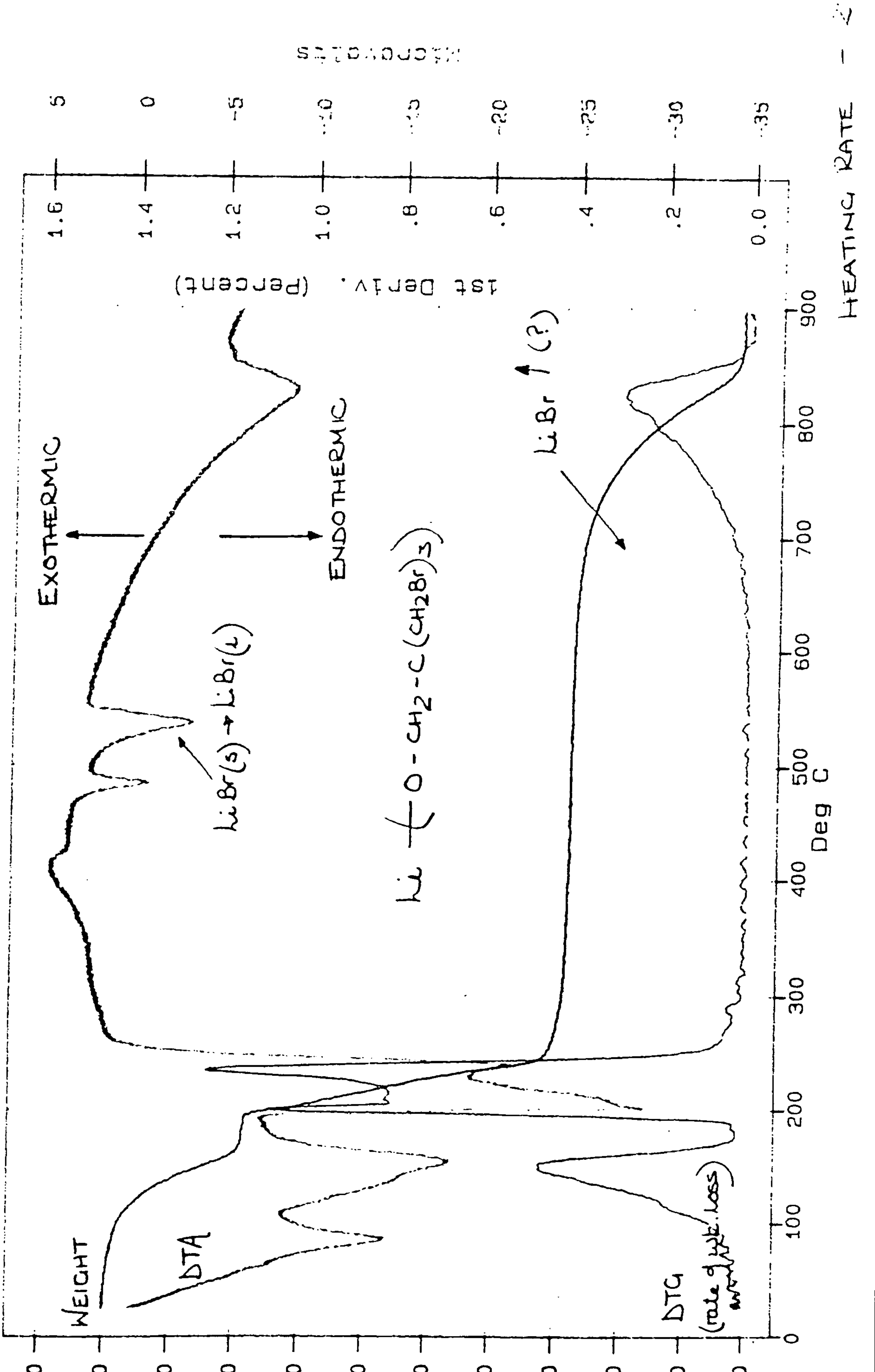
DSC of Zn(OTBN)$_2$



DSC of Ti(OTBN)$_4$



DSC of Mg(OTBN)$_2$



DSC of LiOTBN

APPENDIX B

UNIVERSITY OF DURHAM

Board of Studies in Chemistry

COLLOQUIA, LECTURES AND SEMINARS GIVEN BY INVITED SPEAKERS 1ST AUGUST 1988 to 31st JULY 1989

AVEYARD, Dr. R. (University of Hull) Surfactants at your Surface	15th March, 1989
AYLETT, Prof. B.J. (Queen Mary College, London) Silicon-Based Chips:- The Chemist's Contribution	16th February, 1989
BALDWIN, Prof. J.E. (Oxford University) Recent Advances in the Bioorganic Chemistry of Penicillin Biosynthesis	9th February, 1989
BALDWIN & WALKER, Drs. R.R. & R.W. (Hull University) Combustion: Some Burning Problems	24th November, 1988
BUTLER, Dr. A.R. (St. Andrews University) Cancer in Linxiam: The Chemical Dimension	15th February, 1989
CADOGAN, Prof. J.I.G. (British Petroleum) From Pure Science to Profit	10th November, 1988
CASEY, Dr. M. (University of Salford) Sulphoxides in Stereoselective Synthesis	20th April, 1989
CRICH, Dr. D. (University College London) Some Novel Uses of Free Radicals in Organic Synthesis	27th April, 1989
DINGWALL, Dr. J. (Ciba Geigy) Phosphorus-containing Amino Acids: Biologically Active Natural and Unnatural Products	18th October, 1988
ERRINGTON, Dr. R.J. (University of Newcastle-upon-Tyne) Polymetalate Assembly in Organic Solvents	1st March, 1989
FREY, Dr. J. (Southampton University) Spectroscopy of the Reaction Path: Photodissociation Raman Spectra of NOCl	11th May, 1989
GRADUATE CHEMISTS, (Polytechs and Universities in North East England) R.S.C. Symposium for presentation of papers by postgraduate students	12th April, 1989
HALL, Prof. L.D. (Addenbrooke's Hospital, Cambridge) NMR - A Window to the Human Body	2nd February, 1989
HARDGROVE, Dr. G. (St. Olaf College, U.S.A.) Polymers in the Physical Chemistry Laboratory	December, 1988
HARWOOD, Dr. L. (Oxford University) Synthetic Approaches to Phorbols Via Intramolecular Furan Diels-Alder Reactions: Chemistry under Pressure	25th January, 1988

JÄGER, Dr. C. (Friedrich-Schiller University GDR) NMR Investigations of Fast Ion Conductors of the NASICON Type	9th December, 1988
JENNINGS, Prof. R.R. (Warwick University) Chemistry of the Masses	26th January, 1989
JOHNSON, Dr. B.F.G. (Cambridge University) The Binary Carbonyls	23rd February, 1989
LUDMAN, Dr. C.J. (Durham University) The Energetics of Explosives	18th October, 1988
MACDOUGALL, Dr. G. (Edinburgh University) Vibrational Spectroscopy of Model Catalytic Systems	22nd February, 1989
MARKO, Dr. I. (Sheffield University) Catalytic Asymmetric Osmylation of Olefins	9th March, 1989
McLAUCHLAN, Dr. K.A. (University of Oxford) The Effect of Magnetic Fields on Chemical Reactions	16th November, 1988
MOODY, Dr. C.J. (Imperial College) Reactive Intermediates in Heterocyclic Synthesis	17th May, 1989
PAETZOLD, Prof. P. (Aachen) Iminoboranes $XB\equiv NR$: Inorganic Acetylenes?	23rd May, 1989
PAGE, Dr. P.C.B. (University of Liverpool) Stereocontrol of Organic Reactions Using 1,3-dithiane-1-oxides	3rd May, 1989
POLA, Prof. J. (Czechoslovak Academy of Sciences) Carbon Dioxide Laser Induced Chemical Reactions - New Pathways in Gas-Phase Chemistry	15th June, 1989
REES, Prof. C.W. (Imperial College London) Some Very Heterocyclic Compounds	27th October, 1988
SCHMUTZLER, Prof. R. (Technische Universitat Braunschweig) Fluorophosphines Revisited - New Contributions to an Old Theme	6th October, 1988
SCHROCK, Prof. R.R. (M.I.T.) Recent Advances in Living Metathesis	13th February, 1989
SINGH, Dr. G. (Teesside Polytechnic) Towards Third Generation Anti-Leukaemics	9th November, 1988
SNAITH, Dr. R. (Cambridge University) Egyptian Mummies: What, Where, Why and How?	1st December, 1988
STIBR, Dr. R. (Czechoslovak Academy of Sciences) Recent Developments in the Chemistry of Intermediate-Sited Carboranes	16th May, 1989
VON RAGUE SCHLEYER, Prof. P. (Universitat Erlangen Nurnberg) The Fruitful Interplay Between Calculational and Experimental Chemistry	21st October, 1988
WELLS, Prof. P.B. (Hull University) Catalyst Characterisation and Activity	10th May, 1989

UNIVERSITY OF DURHAM

Board of Studies in Chemistry

COLLOQUIA, LECTURES AND SEMINARS GIVEN BY INVITED SPEAKERS
1ST AUGUST 1989 TO 31ST JULY 1990

BADYAL, Dr. J.P.S. (Durham University) Breakthoughs in Heterogeneous Catalysis	1st November, 1989
BECHER, Dr. J. (Odense University) Synthesis of New Macrocylic Systems using Heterocyclic Building Blocks	13th November, 1989
BERCAW, Prof. J.E. (California Institute of Technology) Synthetic and Mechanistic Approaches to Ziegler–natta Polymerization of Olefins	10th November, 1989
BLEASDALE, Dr. C. (Newcastle University) The Mode of Action of some Anti–tumour Agents	21st February, 1990
BOWMAN, Prof. J.M. (Emory University) Fitting Experiment with Theory in Ar–OH	23rd March, 1990
BUTLER, Dr. A. (St. Andrews University) The Discovery of Penicillin: Facts and Fancies	7th December, 1989
CHEETHAM, Dr. A.K. (Oxford University) Chemistry of Zeolite Cages	8th March, 1990
CLARK, Prof. D.T. (ICI Wilton) Spatially Resolved Chemistry (using Natures's Paradigm in the Advanced Materials Arena)	22nd February, 1990
COLE–HAMILTON, Prof. D.J. (St. Andrews University) New Polymers from Homogeneous Catalysis	29th November, 1989
CROMBIE, Prof. L. (Nottingham University) The Chemistry of Cannabis and Khat	15th February, 1990
DYER, Dr. U. (Glaxo) Synthesis and Conformation of C–Glycosides	31st January, 1990
FLORIANI, Prof. C. (University of Lausanne, Switzerland) Molecular Aggregates – A Bridge between homogeneous and Heterogeneous Systems	25th October, 1989
GERMAN, Prof. L.S. (USSR Academy of Sciences – Moscow) New Syntheses in Fluoroaliphatic Chemistry: Recent Advances in the Chemistry of Fluorinated Oxiranes	9th July, 1990
GRAHAM, Dr. D. (B.P. Reserch Centre) How Proteins Absorb to Interfaces	4th December, 1989
GREENWOOD, Prof. N.N. (University of Leeds) Novel Cluster Geometries in Metalloborane Chemistry	9th November, 1989

HOLLOWAY, Prof. J.H. (University of Leicester) Noble Gas Chemistry	1st February, 1990
HUGHES, Dr. M.N. (King's College, London) A Bug's Eye View of the Periodic Table	30th November, 1989
HUISGEN, Prof. R. (Universität München) Recent Mechanistic Studies of [2+2] Additions	15th December, 1989
KLINOWSKI, Dr. J. (Cambridge University) Solid State NMR Studies of Zeolite Catalysts	13th December 1989
LANCASTER, Rev. R. (Kimbolton Fireworks) Fireworks – Principles and Practice	8th February, 1990
LUNAZZI, Prof. L. (University of Bologna) Application of Dynamic NMR to the Study of Conformational Enantiomerism	12th February, 1990
PALMER, Dr. F. (Nottingham University) Thunder and Lightning	17th October, 1989
PARKER, Dr. D. (Durham University) Macrocycles, Drugs and Rock 'n' roll	16th November, 1989
PERUTZ, Dr. R.N. (York University) Plotting the Course of C–H Activations with Organometallics	24th January, 1990
PLATONOV, Prof. V.E. (USSR Academy of Sciences – Novosibirsk) Polyfluoroindanes: Synthesis and Transformation	9th July, 1990
POWELL, Dr. R.L. (ICI) The Development of CFC Replacements	6th December, 1989
POWIS, Dr. I. (Nottingham University) Spinning off in a huff: Photodissociation of Methyl Iodide	21st March, 1990
ROZHKOV, Prof. I.N. (USSR Academy of Sciences – Moscow) Reactivity of Perfluoroalkyl Bromides	9th July, 1990
STODDART, Dr. J.F. (Sheffield University) Molecular Lego	1st March, 1990
SUTTON, Prof. D. (Simon Fraser University, Vancouver B.C.) Synthesis and Applications of Dinitrogen and Diazo Compounds of Rhenium and Iridium	14th February, 1990
THOMAS, Dr. R.K. (Oxford University) Neutron Reflectometry from Surfaces	28th February, 1990
THOMPSON, Dr. D.P. (Newcastle University) The role of Nitrogen in Extending Silicate Crystal Chemistry	7th February, 1990

UNIVERSITY OF DURHAM

Board of Studies in Chemistry

COLLOQUIA, LECTURES AND SEMINARS GIVEN BY INVITED SPEAKERS
1ST AUGUST 1990 TO 31ST JULY 1991

BELL^{+}, Prof. T. (SUNY, Stoney Brook, U.S.A.) Functional Molecular Architecture and Molecular Recognition	14th November, 1990
BOCHMANN^{+}, Dr. M. (University of East Anglia) Synthesis, Reactions and Catalytic Activity of Cationic Titanium Alkyls	24th October, 1990
BRIMBLE, Dr. M.A. (Massey University, New Zealand) Synthetic Studies Towards the Antibiotic Griseusin-A	29th July, 1991
BROOKHART, Prof. M.S. (University of N. Carolina) Olefin Polymerizations, Oligomerizations and Dimerizations Using Electrophilic Late Transition Metal Catalysts	20th June, 1991
BUSHBY^{+}, Dr. R. (Leeds University) Biradicals and Organic Magnets	6th February, 1991
COWLEY, Prof. A.H. (University of Texas) New Organometallic Routes to Electronic Materials	13th December, 1990
DOBSON^{+}, Dr. C.M. (Oxford University) NMR Studies of Dynamics in Molecular Crystals	6th March, 1991
GERRARD^{+}, Dr. D. (British Petroleum) Raman Spectroscopy for Industrial Analysis	7th November, 1990
HUDLICKY, Prof. T. (Virginia Polytechnic Institute) Biocatalysis and Symmetry Based Approaches to the Efficient Synthesis of Complex Natural Products	25th April, 1991
JACKSON^{+}, Dr. R. (Newcastle University) New Synthetic Methods: α-Amino Acids and Small Rings	31st October, 1990
KOCOVSKY^{+}, Dr. P. (Uppsala University) Stereo-Controlled Reactions Mediated by Transition and Non-Transition Metals	6th November, 1990
PRINGLE^{+}, Dr. P.G. (Bristol University) Metal Complexes with Functionalised Phosphines	5th December, 1990
PRITCHARD, Prof. J. (Queen Mary & Westfield College, London University) Copper Surfaces and Catalysts	21st November, 1990

SCHROCK, Prof. R.R. (Massachusetts Institute of Technology) Metal-Ligand Multiple Bonds and Metathesis Initiators	24th April, 1991
SHAW[+], Prof. B.L. (Leeds University) Syntheses with Coordinated, Unsaturated Phosphine Ligands	20th February, 199
SINN[+], Prof. E. (Hull University) Coupling of Little Electrons in Big Molecules. Implications for the Active Sites of (Metalloproteins and other) Macromolecules	30th January, 1991
SOULEN[+], Prof. R. (South Western University, Texas) Preparation and Reactions of Bicycloalkenes	26th October, 1990
WHITAKER[+], Dr. B.J. (Leeds University) Two-Dimensional Velocity Imaging of State-Selected Reaction Products	28th November, 199

[+] Invited specifically for the postgraduate training programme.