BORON HALIDES AND THEIR CYCLIC DERIVATIVES.

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AUGUST, 1964.

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ACKNOWLEDGEMENTS.

The author is very grateful to the late Dr. A.G. Foster who initially acted as his official supervisor. He also thanks Dr. A. Finch, who supervised all the work carried out, for his invaluable advice and guidance. The author is also indebted to Dr. D. Steele for his continuous and willing help with the spectroscopic investigations.

Thanks are also due to the technical staff of Royal Holloway College, and particularly Mr. B. Smethurst.

The author would also like to express his appreciation to the European Research Office of the U.S. Department of the Army for providing him with a research grant.

ABSTRACT.

An Infra-red study has been undertaken to investigate the mode of association in 2-chloro-1,3,2-dioxaborolan. Comments upon this and the spectrum in general are included. The kinetics for the pyrolysis of the above compound were subjected to a semi-quantitative study, from which it was possible to conclude that the reaction was energetically favourable but sterically hampered.

Attempts were made to prepare cyclic diboron compounds but the results were inconclusive.

The vibrational spectra of certain selected diboron compounds, boron halides and dimethylamine have been studied in detail. The assignment of fundamental modes and some combination bands has been attempted.

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INTRODUCTION.

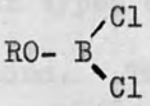
The chemistry of the boron halides began in 1810 with the preparation by Davy of boron trichloride. Since then the field has broadened considerably. All the normal halides BF_3, BCl_3, BBr_3 and BI_3 and the mixed halides[1] BX_2Y ($X = Cl, Br, F;\ Y = Cl, Br, F, X \neq Y$) are known. The existence of BBr_2I and $BBrI_2$ was reported by Besson[2].

In his study of boron halides Stock reported the existence of a subhalide, B_2Cl_4 or diboron tetrachloride, but the yields were poor. When in 1949, Schlesinger, in his search for the hypothetical B_2H_4 discovered a new and more productive route to B_2Cl_4 a whole new series of boron halides became readily available[3].

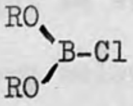
Swartz fluorination of B_2Cl_4 yielded the more stable diboron tetrafluoride[4] and an exchange reaction with BBr_3 produced the tetrabromide[3].

The subiodide has been prepared by passing BI_3 through a radio frequency discharge[5]. Other subhalides obtained by thermal decomposition of B_2Cl_4 have been reported and characterised; B_4Cl_4; B_8Cl_8, the existence of which is now doubtful[6], and $B_{12}Cl_{11}$ which is novel in that it is a free radical[6]. The very small quantities available of the high molecular weight compounds $(BCl)_x$ and $(BI)_x$ have precluded an investigation of their properties. The diboron compounds and their derivatives have recently been reviewed.[7]

Nucleophilic substitution provides a new series of compounds and since the chlorides are the most common and the easiest to study only they are shown below. Compounds of the type I, II and III have been reviewed in the literature on numerous occasions.[8,9,10,11]



I



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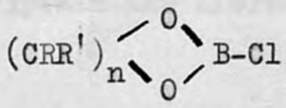
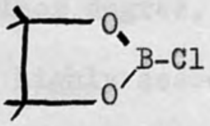


III

R, R' alkyl or aryl n = 2 or 3

They are most easily prepared by reaction between appropriate quantities of the alcohol or glycol and boron trichloride at -80°. The properties of these compounds are dominated, as indeed are those of all boron compounds, by the influence of the vacant $2p_z$ orbital on the boron atom. It is for this reason that the stability of these and the boron subhalide derivatives are so markedly sensitive to the ability of the substituent to partially fill the empty p orbital by back donation of electrons. In the acyclic series II and their cyclic analogues IV

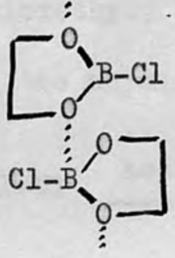


IV

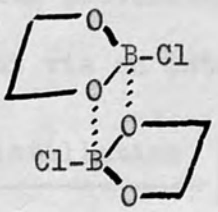
there is a pronounced increase in stability on cyclisation. $(CH_3O)_2BCl$ for example breaks up on distillation but 2-chloro- 1,3,2-dioxaborolan IV, undergoes little decomposition when heated for one hour at 100°[12]

Furthermore type IV compounds are known to exist in a polymeric form in both pure phase and concentrated solution. Both of these properties have been discussed by many authors[12,13,14,15]. It was pointed out[15] that four types of model might be expected to explain the aforementioned association. These are shown below

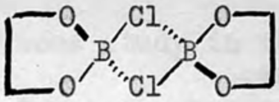
a.



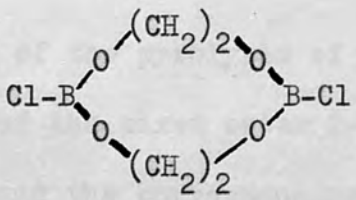
b.



c.

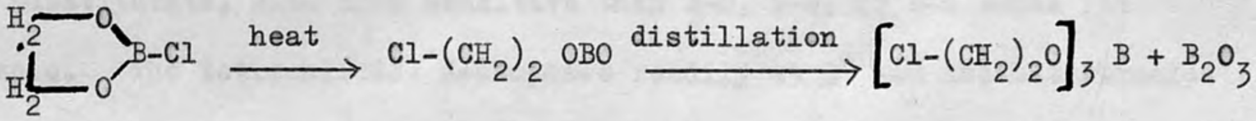


d.

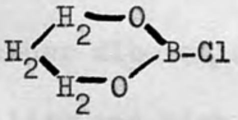


d. is discounted because the degree of association was concentration - dependent and the energy needed for breaking the B-O bonds is not available on dilution. c. is unlikely to explain the mode of association except perhaps to a minor degree, for the n butyl and 2-chlorethyl esters of -olan are also highly associated. 2-chloro- 1,3,2-dioxaborolan possesses a low vapour pressure, high boiling point, and a degree of association certainly greater than two. It was, therefore, suggested that model a. was mainly responsible, though the possibility of the others occuring to a lesser degree was not ruled out. It is noteworthy that except for model d. the boron atom possesses an sp^3 configuration thereby increasing the stability of the compound. In section A of this thesis these possibilities have been examined from the point of view of the infrared spectrum.

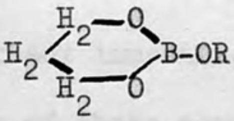
The pyrolysis of 2-chloro- 1,3,2-dioxaborolan was reported by Gerrard et al[12] to yield a pyrolysate which on distillation was identified as tris (2-chlorethyl) borate. The mechanism postulated was similar to that found in the acyclic compounds[8] and went via an intermediate metaborate



In a previous study in this laboratory[16] of the pyrolysis of the six - membered ring 2-chloro- 1,3,2-dioxaborinan V some of the mixed ester 2-(3' chloro-propyl) - 1,3,2-dioxaborinan VI was isolated and the corresponding metaborate VII identified in the pyrolysate



V



VI

$(ROBO)_3$

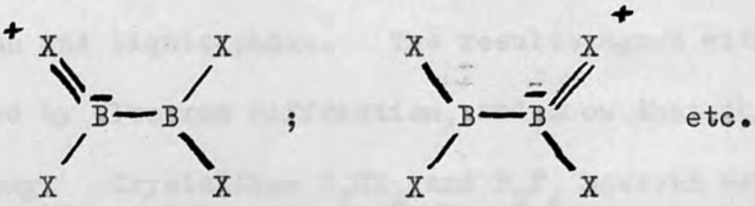
VII

$R = Cl\text{-}CH_2\text{-}CH_2CH_2\text{-}$

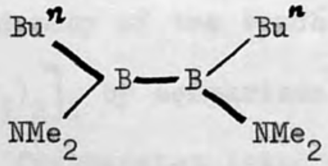
In order to explain the formation of the mixed ester a mechanism which is more complex than that of Gerrards, involving the initial formation of the following intermediate which reacts further with V was suggested

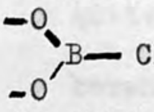
The corresponding mixed ester was not isolated however in the case of 2-chloro-1,3,2-dioxaborolan, though it is knownto be stable, which suggests that for this compound the mechanism is the one proposed by Gerrard. Section A includes a semi-quantitative study of the pyrolysis of this compound.

Very early on in the study of diboron compounds it was apparent that the stability of the B-B bond was very sensitive to the nature of the substituents, much more sensitive than B-O, B-C, or B-N bonds for example. The tetrachloride decomposes readily at 0° and the tetrabromide more readily still. Diboron tetrafluoride however does not decompose appreciably unless heated strongly.[4] Among the derived compounds the esters $B_2(OCH_3)_4$, $B_2(OC_2H_5)_4$ are stable[7] up to 100°, and the amino compounds $B_2[N(CH_3)_2]_4$ is stable[7] in dry air up to 200°. This latter compound is remarkable for it does not react with oxygen even at 100°, whereas the other diboron compounds react immediately even below 0°. The instability and high reactivity of these compounds can most certainly be attributed to the fact that two boron atoms with vacant p orbitals are in juxtaposition, and any substituent which is capable of back donating electrons by an overlap of its filled (lone pair) p orbital with the empty orbital on the boron atom will stabilise the molecule. In boron trichloride π donation occurs from the chlorine lone pairs to the vacant p orbital on the boron atom producing a bond order higher than unity and a bond length shorter than expected[17]. The bond length in B_2Cl_4 is very close to that in BCl_3 which suggests a similar overlap. This being the case the order of reactivity and stability may be understood since resonance structures of the type



will become more important along the series $F < O < N$; $I < Br < Cl < F$. This is supported by the fact that where X does not contain a filled p orbital capable of back donation as in BH_3 and B_2H_4 the molecule does not appear to exist. The ability of X to back donate is probably more important in the diboron compounds than in the boranes since the molecule $B(CH_3)_3$ exists (back donation by hyperconjugation) whereas the corresponding diboron compound could not be prepared. It is of interest to note, however, that Nöth[18] has prepared the alkyl derivative



and confirmed its structure. It would be of further interest to see if in the future tetra alkyl or aryl derivatives can be prepared with strongly electron releasing groups. The stabilising effect of cyclisation on the  moiety prompted a number of attempts to prepare diboron compounds, in which the boron atom was part of a ring. These are included in Section A of this thesis.

Infra-red and raman data on the diboron compounds is sparse or non-existent. Diboron tetrachloride has been studied by Mann et al[19] in the gas and liquid phase. The results agree with those of Hedberg's[20] determined by electron diffraction, and show that the molecule possesses V_d symmetry. Crystalline B_2Cl_4 and B_2F_4 however were shown to be planar[21,22] (V_h symmetry) by x-ray diffraction studies. It is possible that in the crystal there is an intermolecular donation of π electrons permitting the planar structure. Barr[23] observed the infra-red spectrum of diboron tetrafluoride during his studies of the latter compound and diboron tetrachloride but made no assignments.

More recently the infra-red spectrum of this compound was studied in more detail and it was concluded, from a study of the band shapes, that the compound was planar in the gas phase[30]. Becher[24] has assigned many of the bands in the infra-red and raman spectrum of $B_2\left[N(CH_3)_2\right]_4$ by comparison with aminoboranes and with the aid of calculated frequencies based upon a hypothetical B_2N_4 molecule. In the same paper he uses a similar procedure to assign the bands in the spectrum of $B_2(OCH_3)_4$. As a first approximation this procedure is quite good. It does, however, rely upon the assignment of the aminoboranes and ultimately upon dimethylamine. The calculations for this latter molecule were based upon an X_2NH model with an atomic mass of 15 for the atom X. This does not take into account the fact that both CH_3 groups are sterically and electronically connected through the nitrogen atom. It is to be expected therefore that some vibrations will not be localised to the CH_3 group but will instead be coupled. It is not possible to locate these vibrations with certainty without making some allowance for the complexity of the methyl group. A $(CH_3)_2$-NY molecule possesses ten atoms and consequently there are twenty-four normal modes of vibration to be determined. A complete solution would therefore entail handling 24 x 30 matrices, though a reduction can be obtained by setting up the problem in a different form and then making use of the symmetry properties of the molecule. Even then the problem is still long and unwieldy. Crawford[25] has shown how the problem may be considerably simplified for a molecule containing a group, such as the methyl group, that possesses characteristic group frequencies by factorising these from the secular determinant. His procedure may be adapted as follows:-

i. The group in question is considered to be attached to an atom Y of variable mass.

ii. The normal co-ordinates and frequencies are then calculated using a single acceptable set of force constants but with a fresh value for the mass of Y for each determination. Those vibrations which may be described as characteristic of the group will vary little in their frequency and normal co-ordinate. The other frequencies will refer to different vibrations depending upon the mass of the atom or group Y.

There have been numerous investigations of the infra-red and raman spectra of BF_3, BCl_3 and their mixed halides.[1,26,27] BBr_3 has been investigated in the region 3000 - 400 cm.$^{-1}$ of the infra-red and in the raman, but because of the large mass of the bromine atom all but one of the fundamentals are in the far infra-red region and were not observed. Their position however was determined from an analysis of the raman spectrum and combination bands in the infra-red[28]. For identical reasons only one fundamental of boron triiodide appears in the near infra-red but it presents even more difficulties than BBr_3 because the ease with which it decomposes at room temperature precludes a raman study by present techniques. Wentink and Tiensuu[28] gave an assignment for this molecule which they based upon the observation of the single high frequency fundamental and a number of combination bands. More data was obviously necessary for both of these molecules.

Nikitin[29] et al reported the spectrum of $B_2(OH)_4$, $B_2(OD)_4$ and $(BO)_x$. They interpret a band at 1050 cm.$^{-1}$ as the B-B stretch. However, this vibration should not be active in the infra-red for V, V_h or V_d symmetry unless, as they believed, the selection rules are relaxed, and even then one does not expect the band to be so intense as observed. Only four other vibrations have been assigned, the -OH stretch at 3200 - 3400 cm.$^{-1}$, BOH deformations at 875 and 790 cm.$^{-1}$, the BO_2 deformation at 575 cm.$^{-1}$ and the BO stretch at 1320 cm.$^{-1}$. Further assignment they say is not possible without the aid of calculations. It was therefore desirable to re-examine the evidence in the light of previous B_2X_4 calculations.

As previously mentioned B_2Cl_4 possesses V_h symmetry in the crystal. Infra-red and raman data have been confined to the gas and liquid phase. An extension of the infra-red data to the crystal was therefore required as an independent means of confirming the different symmetry proposed by Lipscomb on the basis of x-ray diffraction[21].

DISCUSSION

SECTION A.

Part 1: The infra-red spectrum of 2-chloro-1,3,2-dioxaborolan.

In the previous section it was mentioned that four modes of association have been postulated in order to explain the physical properties of -olan. One method of investigating this which suggests itself is spectroscopic analysis.

The most polar bond in the molecule is boron oxygen followed by boron chlorine and carbon oxygen. It is therefore to be expected that in solvents of different dielectric constant there will be varying degrees of dipole-dipole interaction, which will affect the infra-red spectrum by shifting the frequency of some bands and altering some of the intensities. There are numerous accounts of this type of solvent affects[31-35], but there is as yet no satisfactory quantitative theory[36]. It is not always possible to predict the direction of the shift and in any one molecule there may even be differencies between the vibrations of a group depending upon the symmetry class of the vibration.[35] These shifts do, however, occur, and so an examination of the spectrum of solvated -olan was undertaken with the solvent dielectric constant varying from 2.24 for carbon tetrachloride to 9.08 for dichloromethane. If boron oxygen bridging obtains, then it will be the boron chlorine bond that will take part in strong dipole-dipole interactions and consequently it is to be expected that the boron chlorine modes will suffer the largest shift. Conversely, for boron chlorine bridging boron oxygen modes will shift most. In both cases carbon oxygen bonds will be affected but since the absorption frequency occurs in a different region of the spectrum[38] (c.a. 1100 cm.$^{-1}$) they may be disregarded. Three important points must be kept in mind however. Firstly, the boron oxygen modes are part of a ring vibration. It is not unlikely therefore that the solvent effect will be somewhat reduced in this case. Secondly when the boron chlorine bond stretches the boron atom moves towards the oxygen atoms. Some degree of coupling between B-Cl and B-O stretching modes and the B-Cl stretching and BO_2 deformation modes will result and, depending upon the degree of coupling a reduction in the solvent shift will occur. Since the B-Cl bond lies along the C_2 axis the mixed mode must be of a_1 symmetry if the molecule belongs to C_{2v} point group. Lastly, since an sp^3 boron atom has a higher electronegativity than an sp^2, boron oxygen and boron chlorine bonds will be less polar and the dipole interaction weaker. The result will again be a reduced solvent shift. Despite these difficulties if a solvent of high dielectric constant is used and a shift is observed, boron chlorine bridging is to be expected.

2-chloro-1,3,2-dioxaborolan was prepared by standard procedure[12] and dissolved in pure dry solvents to the required extent. To prevent hydrolysis dry box techniques were used throughout. Cryoscopic measurements carried out in this laboratory[15] showed that the effective state of aggregation in benzene was monomer for a concentration of 0.3% w/v and dimer for 2.4% w/v. At the lower concentration the experimented difficulties were insurmountable on the spectrometer available (Hilger H800). To remove solvent absorptions each spectrum was compensated by working with double beam and using a predetermined amount of the solvent in the reference beam. When path lengths higher than 0.2 mm. were used the compensation became difficult and reduced the signal to noise ratio, and therefore the sensitivity, enormously. As low concentrations demand long path lengths the results for dilute solution were often not reliable. The molecular association is obviously not dependent upon cell thickness, consequently if a change in spectrum accompanies change in path length the data are to be questioned. Such changes were sometimes observed for dilute solutions up to c.a. 0.5% w/v. Another impediment to reliability is the instability of the compound studied. Although room temperature was known and was sufficiently low for the rate of pyrolysis of pure -olan to be insignificant the temperature of the infra-red beam was higher and not easily determined. Minute quantities of impurity from the infra-red cell could also increase the rate of decomposition. At low concentrations the effect could be appreciable. From the observations carried out it was concluded that the instrument was not sensitive enough to give dependable results at low concentrations.

In order to compare the absorption frequencies in various solvents a concentration of 5% w/v was chosen, where the association is probably higher than dimer. Results are shown in Table 1 and Figure 1. Before comparing the frequencies it is relevant to mention the accuracy with which they were determined. Temperature variations within the instrument effect slight distortions of the prism and can be sufficient to throw the marker frequency out by five or on occasions up to twenty wave numbers. These effects could be caused by temperature changes accompanying the weather. It was therefore necessary to run a calibration spectrum of polystyrene before and after each run of -olan. The two correction factors often differed by 5 cm.$^{-1}$, but rarely more. Recorded frequencies could well be out by c.a.± 3 cm.$^{-1}$. In fact the greatest variations occurred at the extremities of the spectrum (3500 cm.$^{-1}$ and 620 cm.$^{-1}$ in the rocksalt region). With this in mind an examination of Table 1 shows no consistent variation. Although there are some changes in the peaks near 1115 cm.$^{-1}$, 1013 and 806 cm.$^{-1}$ these are discounted because they were not monotonic.

No reason is offered for the disappearance of the 806 cm.$^{-1}$ peak in CCl_4.

In order to study the possibility of the variation of intensity with concentration in the process:-

$$\text{monomer} \xrightarrow[\text{-olan concentration}]{\text{increase}} \text{dimer}$$

solutions of -olan in carbon tetrachloride and benzene were prepared, at concentrations varying from 0.45% w/v to 8.5% w/v. Since these solvents both have approximately the same dielectric constant and there is no reason to suspect a different solvation process, the absorption coefficients should be similar. In determining the intensity, corrections were always made for a sloping background by determining average peak heights. The results tabulated in Table 2 are in the form, "peak height per unit percent concentration for a 0.1 mm. path length".

Variations are indeed found and it is interesting to note the repeated absence of the 806 cm.$^{-1}$ peak in CCl_4, but with the previous reservations for dilute solutions only one peak, that at 1360 cm.$^{-1}$, shows a persistent change in both solvents. The variations in the others are not maintained through a complete sequence of concentrations. If the 1360 cm.$^{-1}$ peak were due to an absorption by a B-Cl stretching mode it would indeed be most unusual, since previous assignments for BCl_3, R_1R_2BCl, or R_1BCl_2 molecules have never placed the vibration higher than c.a. 1000 cm.$^{-1}$ - 38, 1, 9, 39, 40.

One of the following explanations is much more likely:-

i) The peak arises from a boron-oxygen stretching mode. It is certainly in the expected region[38,9,39,40]

ii) There is strong mixing between boron-oxygen and boron chlorine stretching modes for the previous reasons.

iii) It is a combination band involving a B-Cl or BO_2 bending mode or a B-Cl stretch as one component.

If iii) applies then one component must show an even greater intensity variation for the fundamental. Later work carried out in this laboratory showed, however, that the B-Cl deformation is expected below 300 cm.$^{-1}$ and so could not be observed on the instrument available. Furthermore the BO_2 deformation only occurred as a minor contribution to other absorptions and a solvent effect would therefore not be expected. If the B-Cl stretch was involved it could only come from a fundamental at 427 cm.$^{-1}$ which was also considerably mixed.

Before deciding upon the two remaining possibilities a more detailed knowledge of the -olan spectrum was thought necessary. To assist in the assignment the fully deuterated analogue of -olan was prepared and its spectrum obtained in solution and pure phase Figures 3 and 4. A comparison between the normal or deuterated compounds with their solution spectra was not easy for their intense absorption necessitates the use of very thin films. Since -olan is very viscous this was difficult and the thinnest films obtained were still far too thick. In general however the solution spectra were quite similar to the pure phase. A comparison of the solution spectra for normal -olan with those for the deuterated species shows a large number of similarities. The peaks around 1250 cm.$^{-1}$ for example, show only minor intensity changes and the 1430 cm.$^{-1}$ band appears with considerable intensity in both. Bands of weak intensity are observed in both near 1100 cm.$^{-1}$ but there is greater intensity for deuterated species. The medium intensity band observed in the deuterated -olan at

1500 cm.$^{-1}$ in the normal species is not observed in the deuterated one. This is probably a CH_2 wagging mode, its position comparing favourably with that for other molecules.

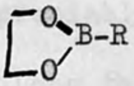
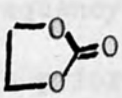
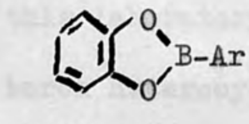
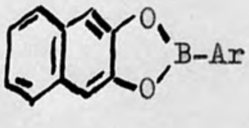
Compound	Ethylene carbonate,	Alkyl Halides
Frequency in cm.$^{-1}$	1480	1440-1470
Reference	42	43

Bellamy[44] attributes intense peaks between 1389 and 1471 cm.$^{-1}$ to methylene groups attached to strongly electronegative groups such as oxygen. Blau et al find similar absorptions in boron compounds[38]. If this peak is due to the methylene group the corresponding CD_2 vibration should be found at c.a. 1000 cm.$^{-1}$. A band is observed near here in the spectrum of the deuterated compound which is not seen in the normal one. It is important to note however that when going from a compound containing the lighter isotope to one with the heavier, the corresponding absorption frequencies usually go down by less than the square root of the mass ratio.

Where the remaining bands are concerned it is difficult to make a reasonable assignment because of the large number of intense absorptions found. In an attempt to find further information the compounds 2-chloro-1,3,2-dioxaborinan and 2-(2'chloroethyl) 1,3,2-dioxaborolan were prepared by standard procedures[12] and their infra-red spectra obtained. Intense peaks common to all the previously mentioned compounds were found in the regions 1430-1480, 1360-1370 and 1220-1250 cm.$^{-1}$.

Lehmann et al have compared the boron oxygen stretching modes in various acyclic borate esters and their derivatives and found them to vary from 1350 to 1450 cm.$^{-1}$ for the antisymmetric vibration and 720 to 1355 cm.$^{-1}$ for the symmetric ones but in the main this latter mode was found between 1230 and 1355 cm.$^{-1}$.

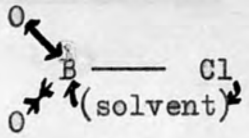
In reference 38 a number of assignments have been made for a series of 1,3,2-dioxaborolan derivatives. Strong bands at 1340 ± 80 cm.$^{-1}$ and at c.a. 1100 cm.$^{-1}$ are attributed to B-O and C-O stretching modes respectively, however their symmetry is not given. A comparison of these and other assignments found in the literature is given below.

Compound	B-O	C-O	Reference
$B(OR)_3$ R=Me, Et, i Pr.	1360-1425 a 1232-1245 s (727 in Me)	1037-1128	45
$Cl\text{-}B(OMe)_2$	1372 a 1277s	1028	45
Cl_2B OMe	1355	1030	45
 R=Cl, O(n Pr) O(i Pr), O(i Bu) O(s Bu), O(n-C_5H_{11})	1340 ± 80	1036 - 1102	38
	-	1076 s, 1125-1180a	42
 	1360-1320 cm.$^{-1}$ a 1060-1140 cm.$^{-1}$ s	1238 ± 4 cm.$^{-1}$ a 1040-1010cm.$^{-1}$ s	46

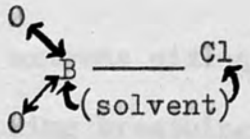
Ar=phenyl,
$pMeC_6H_4$, $pClC_6H_4$
$p\ BrC_6H_4$, o-tolyl

On the basis of this a tentative assignment for the 1430-1480 and 1360 cm.$^{-1}$ bands would be the antisymmetric and symmetric B-O stretch respectively. The bands at 1220 to 1250 cm.$^{-1}$ are somewhat high for the C-O stretch unless there is some coupling with the B-O modes.

If this assignment is correct it is difficult to see why only one of the B-O modes showed a solvent shift unless it is because of the following kinetic energy requirement



antisymmetric
B-O stretch



symmetric B-O
stretch

In the case of the antisymmetric stretch the boron atom is moving perpendicular to the B-Cl bond and the solvent will not hinder this movement appreciably. During the symmetric stretch however, the boron is moving along the line of the B-Cl bond and if the solvent co-ordinates as shown this movement will be hampered. It was thought possible, on completion of this stage, that the B-Cl modes did shift but were at a lower frequency than that covered.

Just prior to the completion of the solvent studies, work was initiated in this laboratory, to calculate the fundamental frequencies of a series of boron heterocyclics[41]. The computations for 2-chloro-1,3,2-dioxaborolan based upon a planar (C_{2v} symmetry) molecule agreed well with the observed spectra. A direct consequence of this is that even when association occurs the dioxaborolan molecules are vibrating as independent species. If B-Cl bridging occurs the chlorine atom will not lie in the plane of the molecule and the agreement between calculated and observed frequencies would have been poor.

The following table gives some of the important results listed in reference 41.

Calculated frequency.cm.$^{-1}$	Symmetry	Type of Vibration
1395	a_1	extreme mixing. Contains ring breathing vibration
1372	b_2	mainly B-O stretch
1246	b_2	mainly C-O stretch
1044	a_1	mainly C-O stretch
427	a_1	mixed vibration containing considerable B-Cl stretch
292	b_2	almost pure OB-Cl deformation.

It is immediately obvious from this that an appreciable solvent shift would only be found below 500 cm.$^{-1}$.

In conclusion it may be said that no evidence for B-Cl bridging was found from the present work, but for confirmation it would be necessary to repeat the investigation on a more reliable instrument and below 500 cm.$^{-1}$ The assignments offered for the CH_2 deformation, B-O symmetric and antisymmetric stretch, and the corresponding C-O vibrations appear to be consistent with other reports.

Table 1. Variation of Frequency with Solvent for 5% w/v solutions.

Carbon Tetrachloride	Benzene	Methylene chloride	Methylene bromide.
1483 v.s.	1486 s	1478 v.s.	1483 v.s.
1431 v.s.	1432 v.s.	1430 v.s.	1430 v.s.
1391 v.s.	1390 s	1393 s	1390 s
1364 v.s.	1365 v.s.	1365 v.s.	1365 v.s.
1327 sh.	1322 sh.	1325 sh.	1321 sh.
1291 v.s.	1293 v.s.	1290 v.s.	1291 v.s.
1260 sh.	1258 sh.	P.R 1237 v.s.	1258 sh.
1240 sh.	1242 sh.		1240 v.s.
1220 v.s.	1222 v.s.		1220 sh.
1175 sh.	N.R	N.R	N.R
1118 w	1119 w	1110 w	1123 w
1066 s	1068 s	1070 s	1070 s
1017 m	1009 m	1010 s	1015 s
945 w	943 w	945 m	947 s
905 w	903 w	902 w	split into 914, 907 m
-	805 m	806 s	812 m
2.238 Dielectric const. at 20	2.284	9.08	7.7 (10°C) 6.7 (40°C)

s = strong
m = medium
w = weak
v = very

N.R - not resolved
P.R. - partially resolved

TABLE 2. Variation of absorbance with concentration.

Freq., cm. $^{-1}$	Carbon Tetrachloride Absorbance/unit % solution and 0.1 mm. path length				Benzene Absorbance/unit % solution and 0.1 mm. path length					
	0.45%	0.75% w/v	5% w/v	7% w/v	0.45%w/v	0.75%w/v	1%w/v	2.4%w/v	5%w/v	8.5%w/v
1480	0.14	0.2	0.22	0.27	(P.R) (0.13)	0.1	(P.R.) (0.065)	0.067	0.094	0.11
1440	0.19	N.R	N.R	0.34	N.R	N.R	N. R	N.R	N.R	N. R
1430	0.19	0.24	0.28	N.R	0.27	0.19	0.2	0.18	0.26 P.R	0.33
1410	0.15	0.15	N.R	N.R	N.R	0.2	0.19	0.092	0.14	N.R
1385	0.098	0.089	0.14	0.19	P.R	N.R	N.R	0.071	0.10	0.22
1360	0.13	0.17	0.24	0.29	P. R	0.13	0.18	0.17	0.22	0.34
1290	0.13	0.17	0.13	0.17	0.11	0.21	0.25	0.24	0.16	0.33
1260	N.R but for a peak at 1242	N.R but for a peak at 1232	0.17	0.23	0.18	0.47	0.58	0.35	0.32	O.S
1236			0.18	0.23	0.18	0.44	0.59	0.33	0.36	O.S
1220	0.17	0.16	0.22	0.26	N.R	N.R	N.R	0.16	0.22	O.S
1070	0.042	0.047	0.1	0.13	0.085	0.047	P.R	0.067	0.10	0.21
1012	0.044	0.04	0.04	0.052	0.067	0.094	0.08	0.062	0.048	0.071
945	0.022	0.27	0.02	0.026	0.018	0.033	0.05	0.031	0.028	0.099
803	-	-	-	-	0.033	0.113	0.12	0.087	0.064	0.094
	*	*		*		*				*

N.R - not resolved P.R - partially resolved O.S peak maximum off scale and intensity not determinable

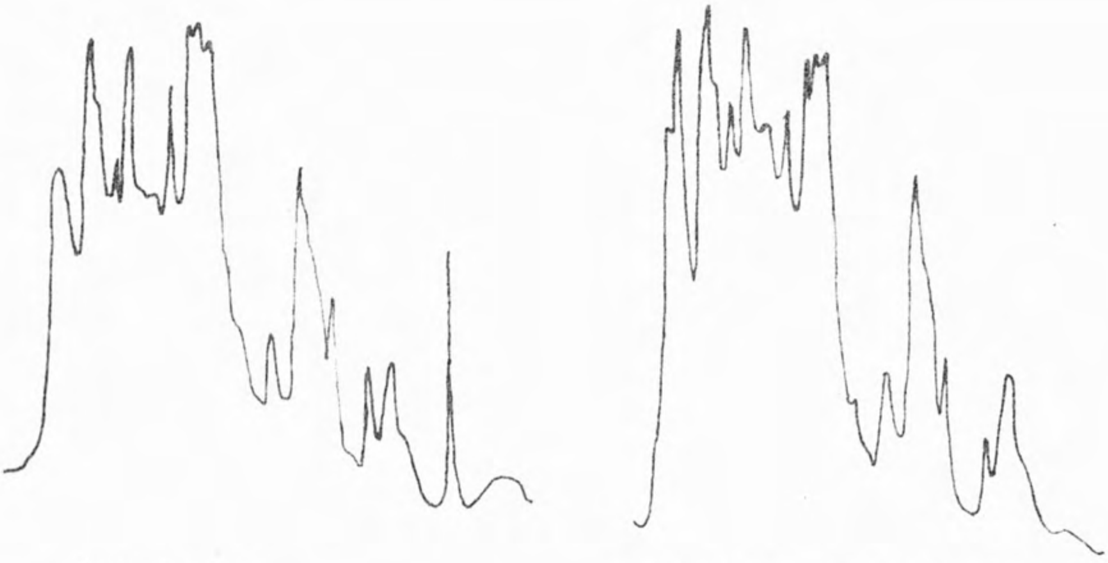
* - values calculated from path lengths other than 0.1 mm.

TABLE 3.

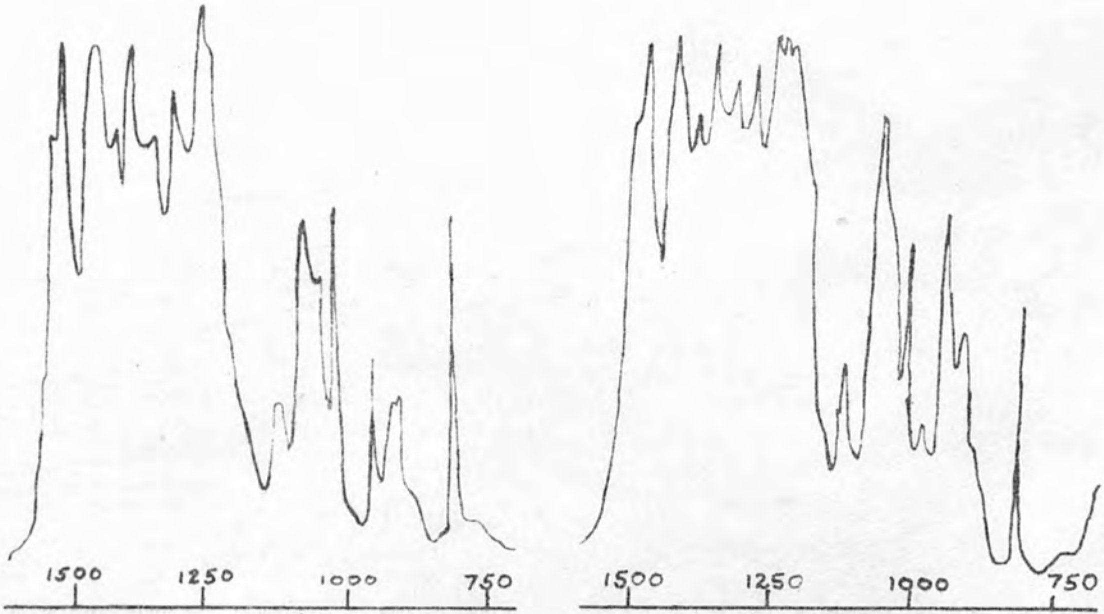
FREQUENCY OF LINES APPEARING IN THE SPECTRA.

Ethylene Glycol	Ethylene d_4 Glycol	2,Chloro 1,3,2 dioxa-borolan	2,Chloro 4,5-tetra deutero 1,3,2 dioxa borolan	2,Chloro 1,3,2 dioxa-borolan 0.3% w/v in ben-zeme 0.2 mm. cell	2,Chloro 1,3,2 dioxa borolan 2.4% w/v in benzene 0.1 mm. cell	2,Chloro 4,5-tetra deutero 1,3,2 dioxa borolan 2.4% w/v in benzene 0.1 mm.cell	2-Chloro 1,3,2-dioxa borinan 5.5% w/v benzene	2(2' chlor-ethyl) 1,3,2-dioxa borolan (C) at dimer cone. 7.5% w/v benzene.
3330 s	3330 s	2942 s	2636 m	2923 w	2997 m	2923 w	1500 s	1500 s
2943 m	2790 w	2897 sh.	2240 s	2888 w	2960 m	2849 v.w.	1453 v.s.	1450 v.s
2877 m	2214 m	1500)broad	2152 m	2728 v.w	1500 m	2740 w	1350 m	1425 v.s
1655 w	2140 w	to) band	2113 s	1490 w	1436	2238 w	1311 sh	1358 v.s
1457 m	2097 m	1200) v.s	2030 w	1432 m	1419 s	2114 v.w.	1299 v.s	1312 s
1410 m	1378 m	1170 sh	1857 w	1407 m	1394 m	1719 v.w.	1264 sh	1265 s
1368 sh.	1195 m	1117 s	1710 w	1360 sh.	1365 s	1499 w	1230 v.s	1250 s
1330 m	1118 m	1150 v.s	1500)Broad	1338 w	1296 s	1453 sh.	1210 sh	1212 sh
1256 w	1105 sh.	975 w	to)band	1326 sh.	1258 v.s.	1431 s	1144 s	1120 m
1205 w	1060 m	931 sh.	1320) s	1288 w	1244 v.s	1346 s.m.	1063 m	1090 sh
1087s	979 m	903 s	1250 s	1252 m	1225 sh.	1323 sh.	937 m	1070 m
1043 s	967 sh.	801 w	1210 sh.	1236 m	1115 w	1302 s	757 s	1032 m
926 s	945 sh.	665 sh.	1160 sh.	1075 w	1062 m	1262 v.s	627 sh	955 m
908 sh.	900 w	652 s	1145 s	1007 v.w	1005 m	1245 sh.	605 s	763 m
	757 m		1116 sh.	939 v.w	942 w	1215 m	547 m	697 m
	737 sh.		1106 sh.	892 v.w	900 w	1175 v.w	455 m	653 m
			990 sh.	800 w.	807 m	1120 sh.	381 w	
			990 s			1095 sh.		
			913 sh.			1085 m		
			801 s			1047 v.w		
			770 sh.			989 m		
			713 w			971 w		
						914 v.w		
						800 m		

s = strong
m = medium
w = weak
v = very



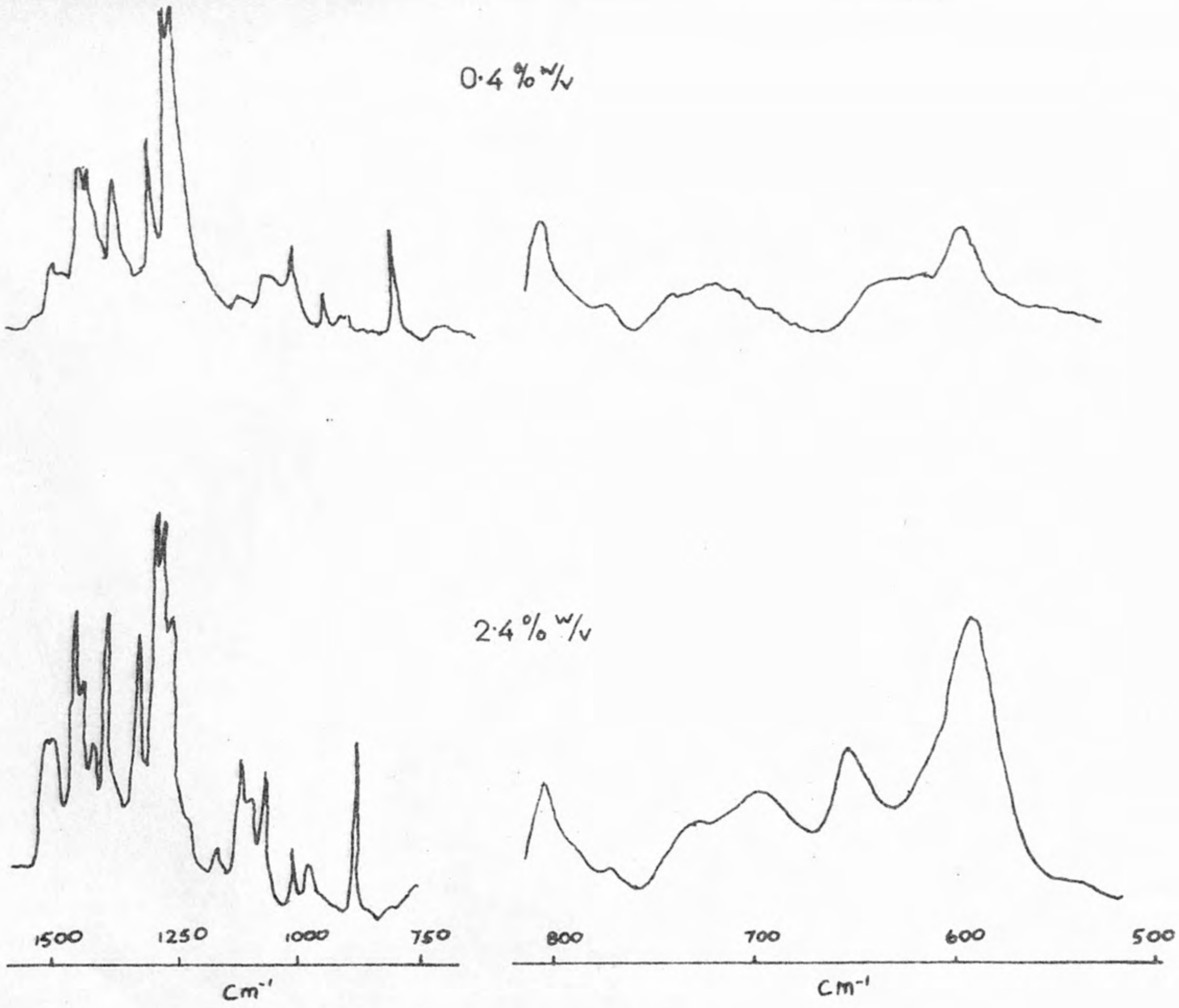
benzene carbon tetrachloride



methylene chloride methylene bromide

c.a. 5% solutions of 2-chloro-1,3,2 dioxaborolan

Fig.1.



benzene solutions of 2-chloro-1,3,2-dioxaborolan

fig. 2.

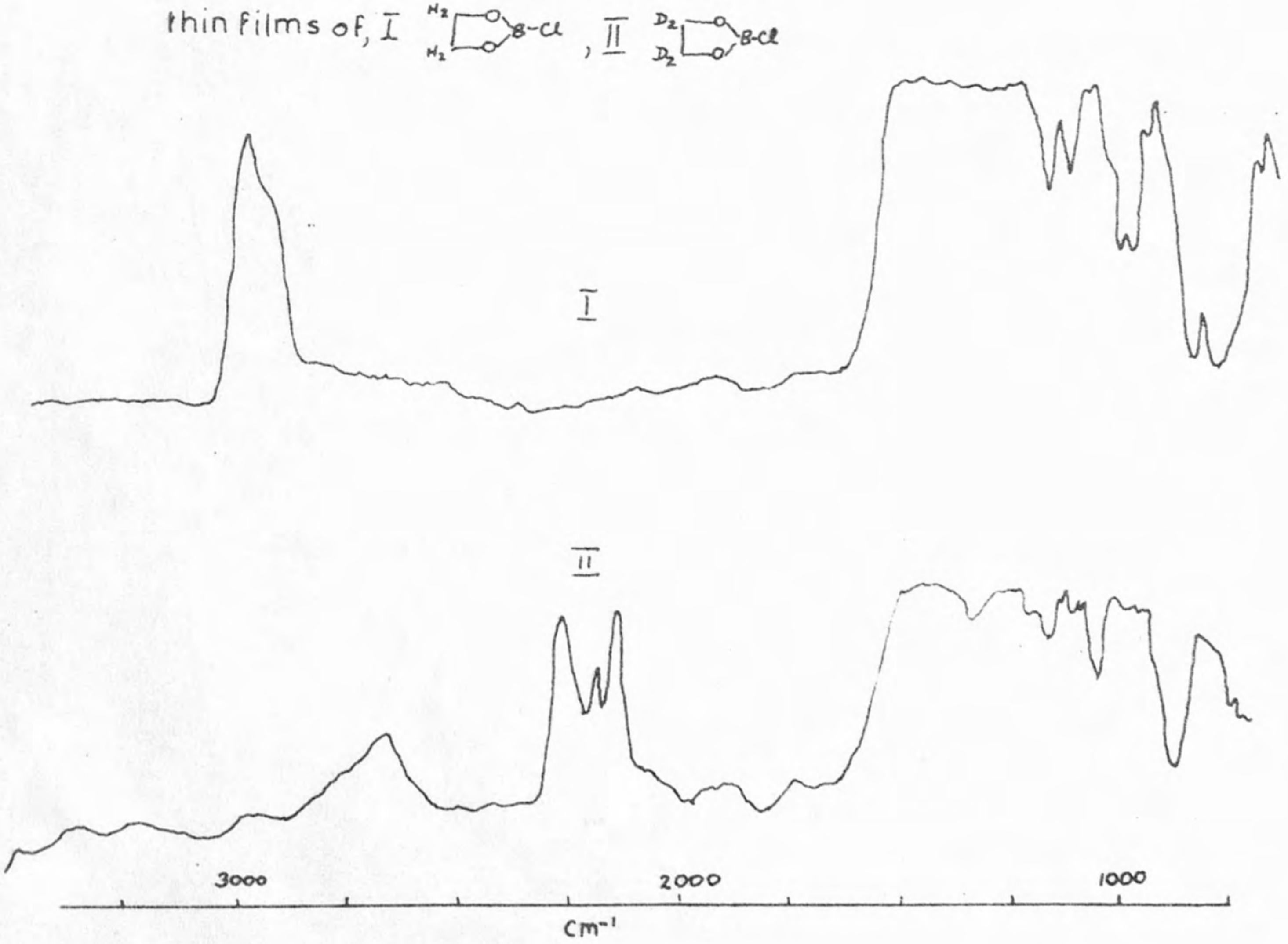

thin films of, I , II

Fig. 3.

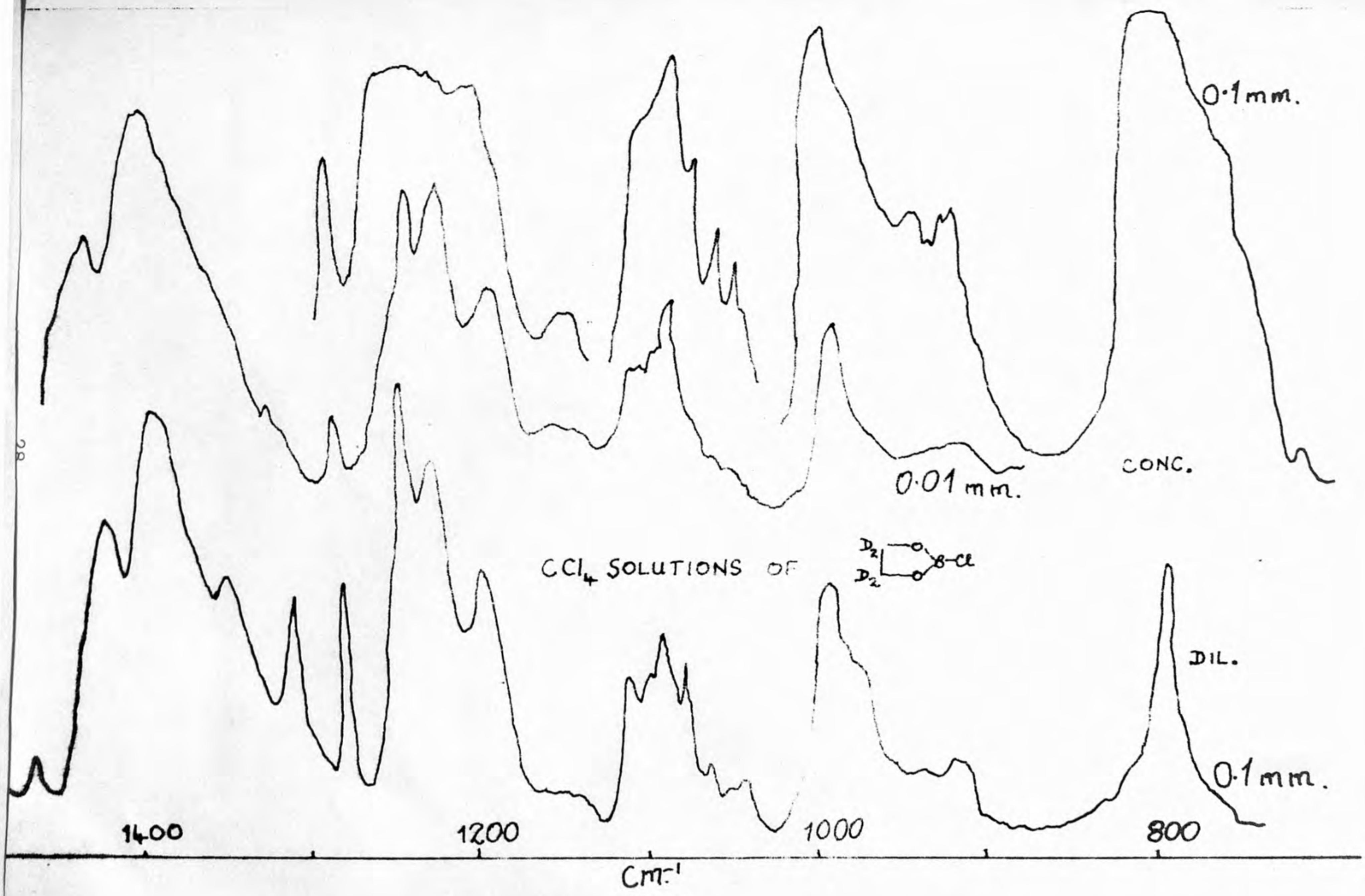
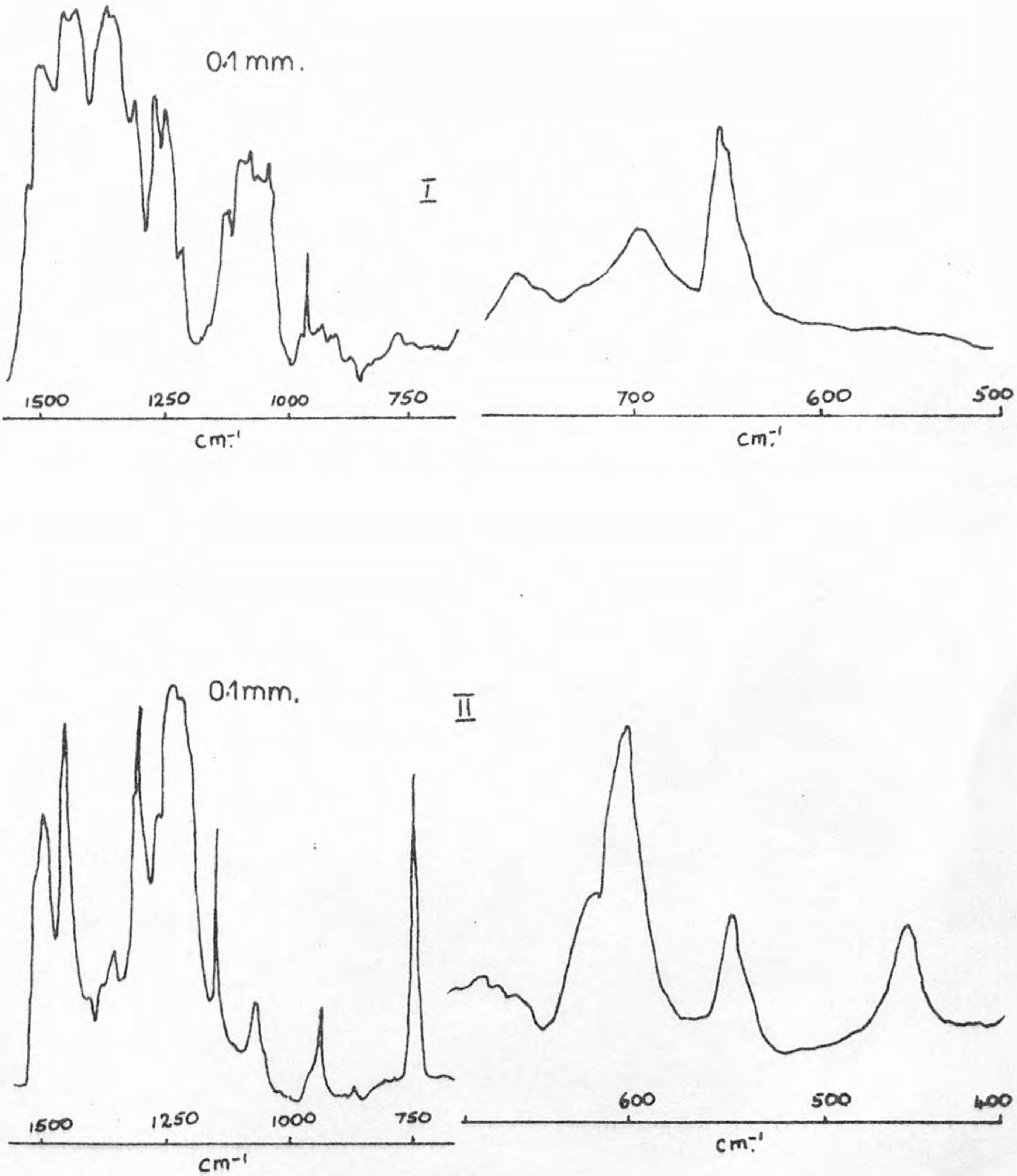

0·1 mm.
CONC.
0·01 mm.
CCl$_4$ SOLUTIONS OF
D$_2$ D$_2$ Cl
DIL.
0·1 mm.
1400
1200
1000
800
Cm⁻¹

Fig. 4.

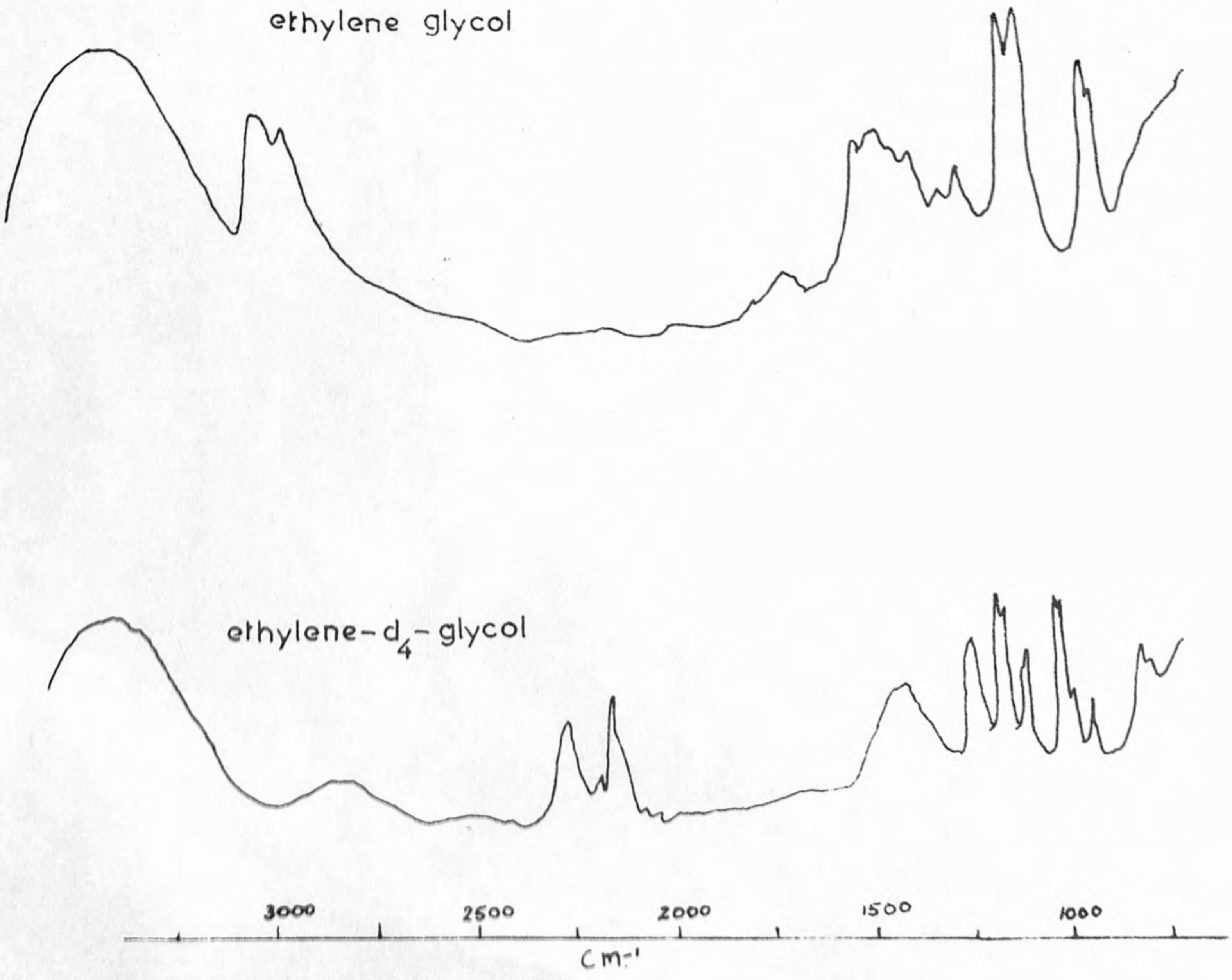


benzene solutions of, I 2-(2'-chloroethyl)-1,3,2-dioxaborolan,

II 2-chloro-1,3,2-dioxaborinan, c.a. 3% w/v

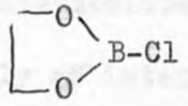
Fig.5.

fig.6.


ethylene glycol
ethylene-d_4-glycol
3000
2500
2000
1500
1000
cm⁻¹

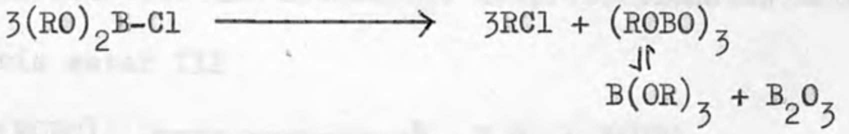
Part 2. Pyrolysis of 2-chloro-1,3,2-dioxaborolan.

1,3,2-dioxaborolan derivatives were first studied in detail by Blau et al[12,47]. The 2-chloro derivative I



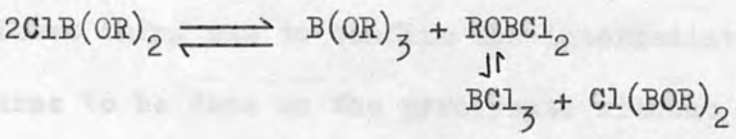
I

is surprisingly stable when compared with the acyclic analogue $(CH_3O)_2B\text{-}Cl$. When heated at 120° for 2 hours in the presence of a trace of Lewes acid ($FeCl_3$) I only underwent 31% decomposition, whereas the dimethoxychloroboronate is very readily decomposed under similar conditions.[47] The decomposition of haloboronates follows one of the reactions below[48]



$$3(RO)_2B\text{-}Cl \longrightarrow 3RCl + \underset{B(OR)_3 + B_2O_3}{\underset{\upharpoonleft\downharpoonright}{(ROBO)_3}} \qquad 1$$

$$3RO_2BCl \longrightarrow B(RO)_3 + B_2O_3 + 3HCl + 3(\text{olefin}) \qquad 2$$

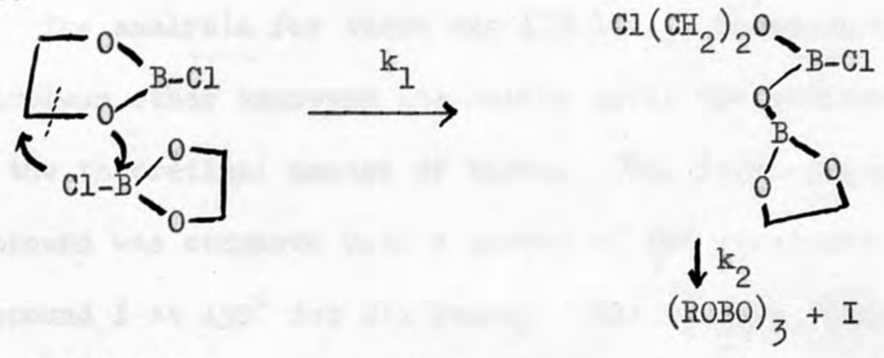


$$2ClB(OR)_2 \rightleftharpoons B(OR)_3 + \underset{BCl_3 + Cl(BOR)_2}{\underset{\upharpoonleft\downharpoonright}{ROBCl_2}} \qquad 3$$

Reactions 1 and 2 occur under pressure or at high temperatures, Reaction 3 is observed under reduced pressure.

Blau et al[12] found that when I was heated under the conditions described above and then subsequently distilled tris(2-chloroethyl) borate was produced. It was assumed that the stoichiometry was similar to Reaction 1. In another reaction at a higher temperature a trace of ethylene was produced. The mechanism was not studied further.

It was decided to investigate the pyrolysis more thoroughly by following the reaction kinetically and if possible to isolate or identify the postulated intermediate metaborate II. The first step in the reaction is probably an intermolecular chlorination followed by a C-O bond cleavage:-



4

$R = Cl-(CH_2)_2-$ II

On distillation the metaborate disproportionates into boric oxide and the tris ester III

$$(ROBO)_3 \rightleftharpoons B_2O_3 + \underset{III}{B(OR)_3}$$

The first thing was to confirm the intermediate metaborate. This had of course to be done on the pyrolysate without purification. 2-chloroethyl metaborate was prepared independently by two methods[49]. In the first pure 2-chloroethanol and boric acid were mixed in the required proportions and the water produced during reaction was removed by azeotropic distillation. The product showed the characteristic metaborate peaks[50] in the infra-red at 720 and 735 cm.$^{-1}$, but the analysis of the boron content was low by 20%. In the second attempt, tris (2-chloroethyl) borate was first prepared from the corresponding alcohol and boric acid and purified by fractional distillation. The borate analysed to within 0.5% of the theoretical value. Metaborate was then prepared from the borate and boric oxide by refluxing the mixture. The product was washed with CH_2Cl_2 and dried.

$$3ROH + 3H_3BO_3 \rightleftharpoons (ROBO)_3 + 6H_2O$$

$$(RO)_3B = B_2O_3 \rightleftharpoons (ROBO)_3$$

The analysis for boron was 17% low. Successive washings with petroleum ether improved the purity until the metaborate possessed 99% of the theoretical amount of boron. The infra-red spectrum of this compound was compared with a sample of the pyrolysate obtained by heating compound I at 150° for six hours. The spectra (figure 7) were identical but different to that of I or III.

It was originally desired to study the solution kinetics of reaction 4 by following the disappearance of I and the formation of II in a solvent. For this, a solvent possessing three properties was required

a) to dissolve I and II without reacting or forming an adduct with them.

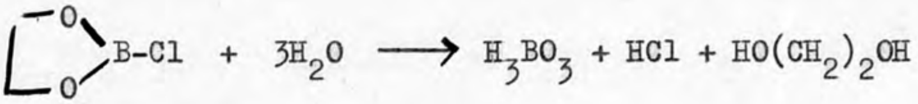
b) to have a high boiling point ($> 100^\circ$)

c) to be "clear in the infra-red from 600 - 800 $cm.^{-1}$

The usual solvents, benzene, CCl_4, CH_2Cl_2, paraffins, ethers, etc. were found unsuitable for one or other of the above reasons. Basic nitrogen compounds would obviously react but it was thought that if the nucleophilic power of the nitrogen could be reduced considerably a suitable solvent might be found. Nitrobenzene was first tried but it was found to have an absorption peak in the infra-red which almost overlapped those of the metaborate. The nitrogen atom in dimethylformamide is not a strong nucleophile[51,52] and so this compound was considered as a possible solvent. The boiling point (153°) and infra-red were suitable but on mixing with I an immediate reaction took place and the white solid which separated out was filtered off. The substance was easily hydrolysed and unlike the starting materials was insoluble in benzene. An infra-red spectrum showed a $C=O$ absorption in the same region as dimethylformamide (1680 cm.$^{-1}$). An analysis for boron and easily hydrolysable chlorine indicated the possibility of a 1:1 adduct. If an adduct is formed the question is; where does the boron co-ordinate, to oxygen or nitrogen? Gerrard[9] discusses this in some detail for amide complexes with boron trihalides and favours the co-ordination to oxygen from parachor and n.m.r. evidence.

It was decided to continue by pyrolysing I in the absence of solvent. This is perhaps unsatisfactory since the medium is constantly changing but a previous study in this laboratory[14] had shown that 2-chloro-1,3,2-dioxaborinan obeyed 2nd order kinetics over 70% decomposition when pyrolysed at 100° under these conditions.

For each kinetic run about 0.3 - 0.5 g of I were accurately weighed into glass ampules or 10 ml. B10 flasks and the containers sealed or securely stoppered. The complete operation, except for the sealing, was carried out in a dry box. After selected time intervals an ampule would be withdrawn from the constant temperature bath cooled quickly to room temperature or below and then cleaned thoroughly. The ampule was then broken under c.a. 1 inch of water in a conical flask. The pyrolysate which contains I and metaborate II hydrolyses immediately to aqueous HCl, boric acid, ethylene glycol and 2-chloroethanol as follows



$$(ROBO)_3 + 6H_2O \longrightarrow 3ROH + 3H_3BO_3$$

The HCl was titrated with $\frac{N}{10}$ NaOH using a methy red indicator and from this the amount of undecomposed I determined. This procedure was checked by determining the total boron content on some runs with a caustic-soda mannitol titration. If the procedure is reliable, as it was in fact found, the % boron will be the same as in I.

The pyrolysis was followed at three temperatures, 100°, 116° and 150° c.a. For the 100° run the ampules were placed in boiling water, (99.5±0.3°), the 150° bath consisted of a large Jacksen condenser with a water cooled condenser fitted to a side arm. Ethylene glycol was placed in the well of the Jacksen and the vapour from boiling anisole was used to heat the well (cf. figure 8). The temperature of the glycol rose to 153.6° within an hour and never varied by more than ±0.2°.

The 116° bath contained high boiling oil which was heated by gas rings to 100° and an electrical heater controlled by a mercury regulator supplied sufficient heat to raise the temperature the extra 6° and keep it at $116 \pm 0.5^{\circ}$.

The results were tested for 1st, 2nd and 3rd order kinetics by plotting the following functions of (a-x) - i.e. the remaining moles of undecomposed I - against time. Where "a" is the number of moles I initially and x the number of moles I decomposed after time t.

1st order	$\log_{10}(a-x)$ vs. time
2nd order	$\frac{1}{(a-x)}$ vs. time
3rd order	$\frac{1}{(a-x)}$ vs. time

Only the second order plots gave a reasonable straight line, and are reproduced in figure 9. The data for these plots are given in Table 4 and were derived as though the starting material was always <u>one</u> mole of pure 2-chloro- 1,3,2-dioxaborolan, i.e. a=1 in (a-x). Included in figure 9 are corresponding plots of I + BCl_3. Although each plot has been drawn as a continuous straight line, it was found that after a certain time the rate appeared to increase sharply. In fact, after the last experimental point shown on each line it may be assumed that this occurs. It is possible that the rate constant changes with the medium or that there is a different order for the reaction. What is certain, however, is that since the medium changes more drastically as the reaction proceeds, the rate equations become less and less reliable, and are probably meaningless before 50% decomposition is reached. For this reason these points have not been plotted.

In order to follow the production of metaborate a specially designed heated infra-red cell was built and is shown in figure 10. The main body of the cell was made from a brass cylinder with slots cut inthe end plots to hold the KBr windows. Both sections of the holder were heated electrically by two layers of nichrome wire and insulated with asbestos paper. The temperature of the sample was obtained by using a copper constantin thermocouple embedded in the cell windows. Before each run the cell was heated to the required temperature and allowed to equilibrate for one hour. The cell was then placed in the sample beam of an infracord 137 spectrometer. Pure I was injected into the cell through one of the inlets, and these then sealed with P.T.F.E. plugs. Every fifteen minutes the spectrum was scanned from 700 - 800 cm.$^{-1}$.

The intensity I of the metaborate peak is related to the concentration "C" by Beers law

$$\log I_0/I \quad = \quad \epsilon\, c\, d \ldots\ldots\ldots\ldots (1)$$

where d is the path length, ϵ the absorption coefficient and I_0 the original beam intensity.

The second order plot may be obtained as follows:-

$$kt \quad = \quad \frac{1}{(a-x)} \qquad \text{where k is the rate constant}$$

$$\text{i.e.} \quad k(a-x) \quad = \quad 1/t$$

if the intensity at time t^1 is I^1.

Then using (1) a plot of $1/t^1$ vs $\log_{10} I^1$ will be a straight line. In theory it should be possible to obtain a rate constant, however, though it may be possible to find most of the unknowns in .... (1)

the constant ϵ was not so susceptible. Extrapolations from solution spectra were not possible since the metaborate was insoluble in all the solvents tried. It did not even appear to dissolve in compound I. Determinations in the solid phase are useless since ϵ is almost certainly different under the conditions of pyrolysis - indeed solid phase determinations would have to be carried out for different concentrations of metaborate in KBr discs. Therefore, k could not be obtained from the intensity measurements.

Figure 11 shows the spectra obtained and figure 12 the order plot. The data are given in Table 5.

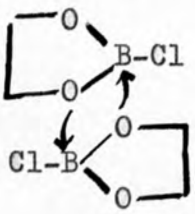
According to the Arrhenius equation the rate constant k depends upon the temperature T. $k = Ae^{-\Delta E/RT}$

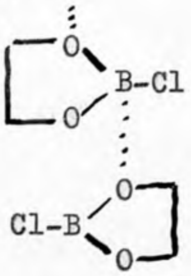
A plot of $\log_e k$ against $1/T$ should be a straight line of slope $-\Delta E/R$, where E is the activation energy and R the gas constant. For convenience $\log_{10} 10k$ was plotted against $1/T \times 10^3$ (cf. figure 13). The activation energy was found to be c.a.-10 ± 3 K cals. mole^{-1}. This value is extremely low and would indicate that the reaction was so facile at room temperature that the compound was unlikely to exist, unless it is sterically prevented or hampered from reacting. The pre-exponential factor A is related to the entropy of activation as follows

$$A = e^{\Delta S/R}$$

Using this an entropy of approximately -45 ± 15 e.u. was calculated. This is indeed far more negative that is usually encountered and would indicate that the reaction is sterically very unfavourable. As previously mentioned compound I is associated in the pure phase and in benzene solution.

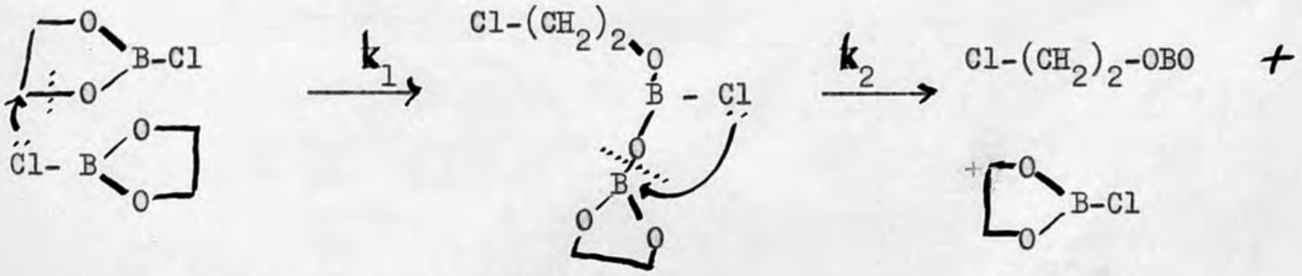
The most probable modes were given as





Now the rate controlling step during the pyrolysis is most likely to be chlorination of the carbon atom. This is supported by the catalytic effect of BCl_3. Therefore under conditions of maximum association pyrolysis should occur. Such conditions will be the pure phase and at a temperature at which the intermolecular bonds are stable. Pure 2-chloro 1,3,2-dioxaborolan does indeed decompose at room temperature, but if one assumed that the rate of reaction dropped by approximately 50% for a 10° drop in temperature, then the rate at room temperature should be extremely slow. As the temperature increases the intermolecular bonds are ruptured and are probably non-existent at 100°. Under these conditions reaction will only occur between molecules that are favourably orientated and a low entropy would be expected. Furthermore since the acyclic chloroboronates are so unstable the chlorination of the carbon atom is probably relatively easy and with a low energy of activation. It must be emphasised, however, that though the picture is likely to be qualitatively correct and the approximate values given for the energy and entropy of activation are of the expected magnitudes the actual values are probably not reliable. This arises from the very nature of the kinetic laws, which certainly apply in the gas phase and dilute solution and are theoretically meaningful under these conditions, but in the pure phase and with a constantly changing medium their application becomes somewhat questionable. Furthermore, for a compound such as this where the pyrolysis is sensitive to impurities it is important to have some physical means such as boiling point or melting point for testing the purity, but only the boron and chlorine analyses were used as an easy check, and these will only be sensitive to about 0.5%. Since the infra-red data on the metaborate formation confirmed that obtained by analysis of easily hydrolisable chlorine it would be of interest to repeat this work in any solvent which can be heated to 150° without boiling, decomposing or interacting with the solute. If the molecular weight can be determined at different temperatures, say ebullioscopically [illegible] the point at which only monomer exists could be measured.

In conclusion it has been shown that the pyrolysis of 2-chloro- 1,3,2-dioxaborolan follows second order kinetics up to approximately 20% decomposition and that the mechanism for the reaction most probably involves initial chlorination of a carbon atom to form some intermediate which on decomposition produces the metaborate.



The kinetics imply that $k_1 \gg k_2$

TABLE 4: PYROLYSIS DATA FOR 2-CHLORO-1,3,2-DIOXABOROLAN.

Temperature 153.5°

Time hr.	$\frac{1}{(a-x)}$ moles^{-1}
0.25	1.080
0.5	1.101
1	1.252
1.5	1.330
1.87	1.429
2.25	1.478

$k = 0{\cdot}220$ moles^{-2} hr.$^{-1}$

Temperature 116.5°

Time	$\frac{1}{(a - x)}$
0.5	1.041
1.0	1.125
1.5	1.160
2.0	1.267
2.5	1.289
3.0	1.340
3.5	1.436

$k = 0{\cdot}122$ moles^{-2} hr^{-1}.

Temperature 100°

Time	$\frac{1}{(a - x)}$	Time	$\frac{1}{(a - x)}$	Time	$\frac{1}{(a - x)}$
3	1.095	0.75	1.038	0.75	1.052
4	1.154	1.25	1.157	1.25	1.093
5	1.193	1.75	1.086	1.75	1.118
6	1.220	2.25	1.105	2.25	1.155
7	1.276	2.75	1.137		
8	1.300				

$k = 0{\cdot}038$ moles^{-2} hr^{-1}.

TABLE 5

PYROLYSIS OF 2-CHLORO-1,3,2-DIOXABOROLAN

INFRA-RED DATA.

Temperature 100±1°

Time. hour.	Intensity (% Transmission) $735\ cm.^{-1}$	$720\ cm.^{-1}$
0.25	0.55	9
0.5	17	21
0.75	32	37
1	38	43
1.5	49	52
2	53	58
2.5	57	62
3	60	63
3.5	65	68
4	66	69
4.5	67	70

Cell thickness 0.1 mm.

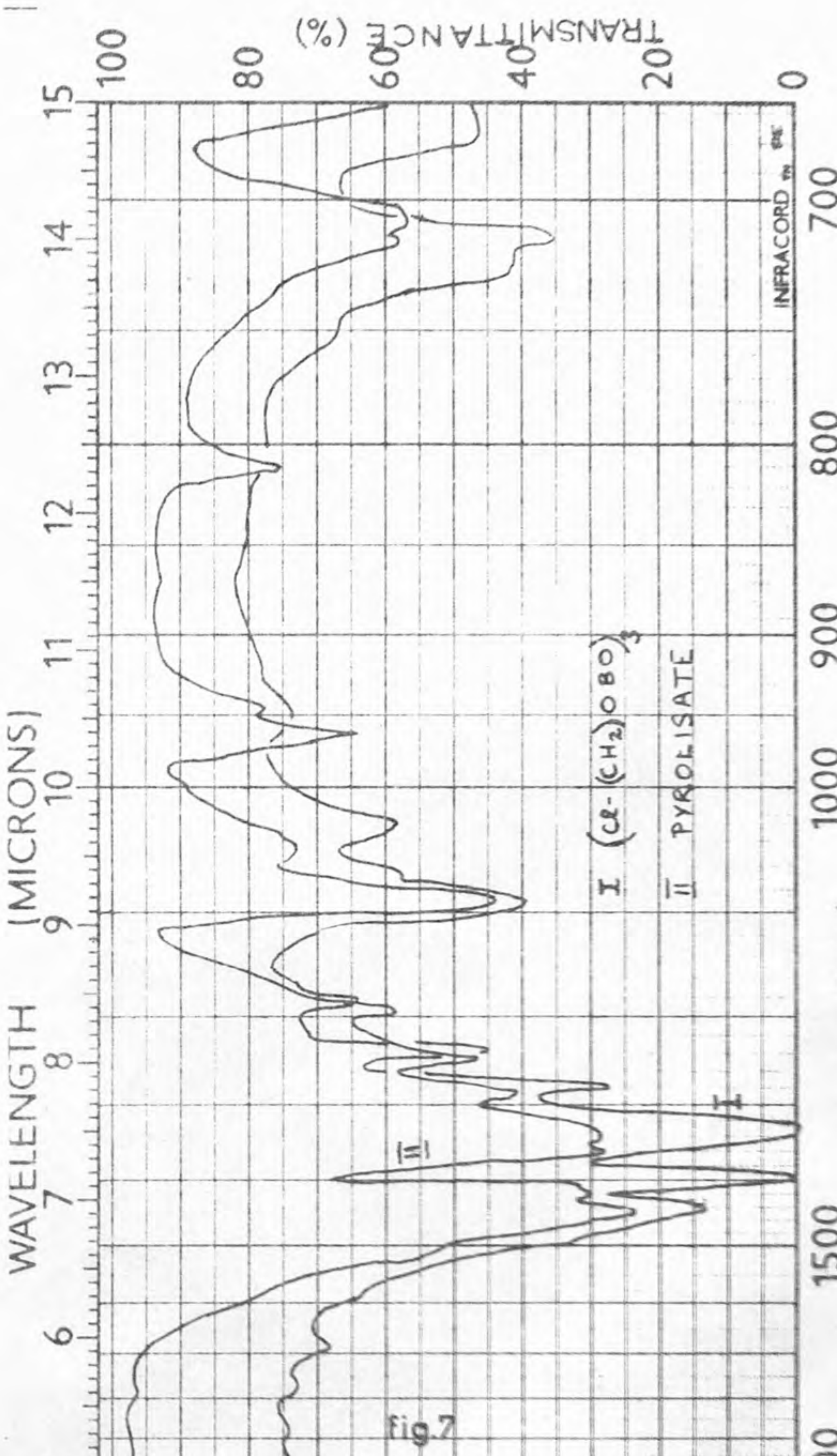


fig.7
WAVELENGTH (MICRONS)
5
6
7
8
9
10
11
12
13
14
15
TRANSMITTANCE (%)
100
80
60
40
20
0
CM⁻¹
2000
1500
1000
900
800
700
INFRACORD
I
II
I (Cl-(CH₂)OBO)₃
II PYROLISATE

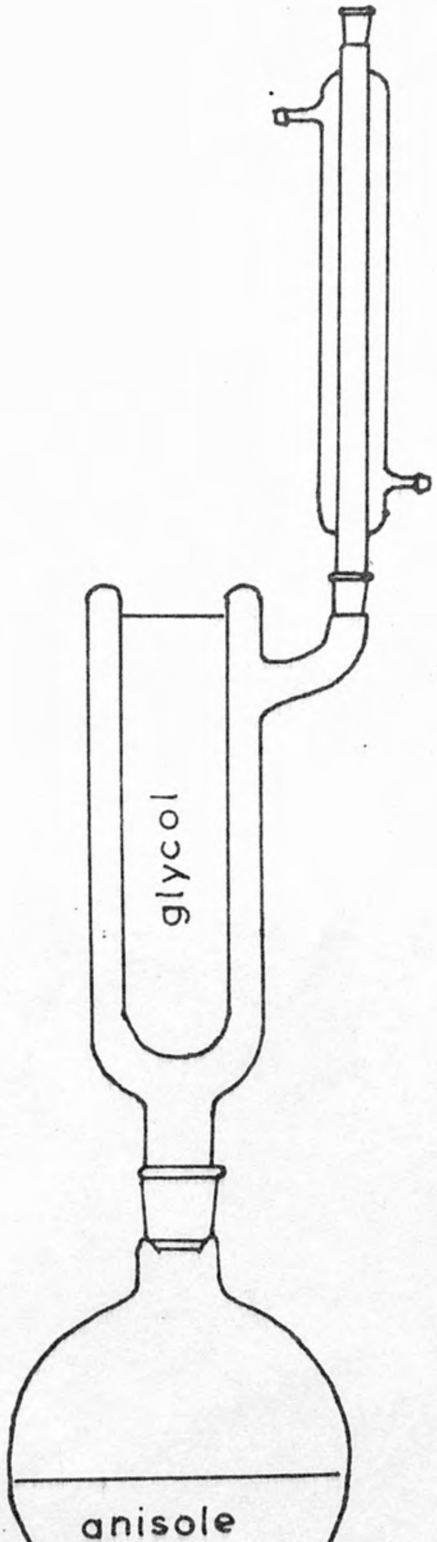
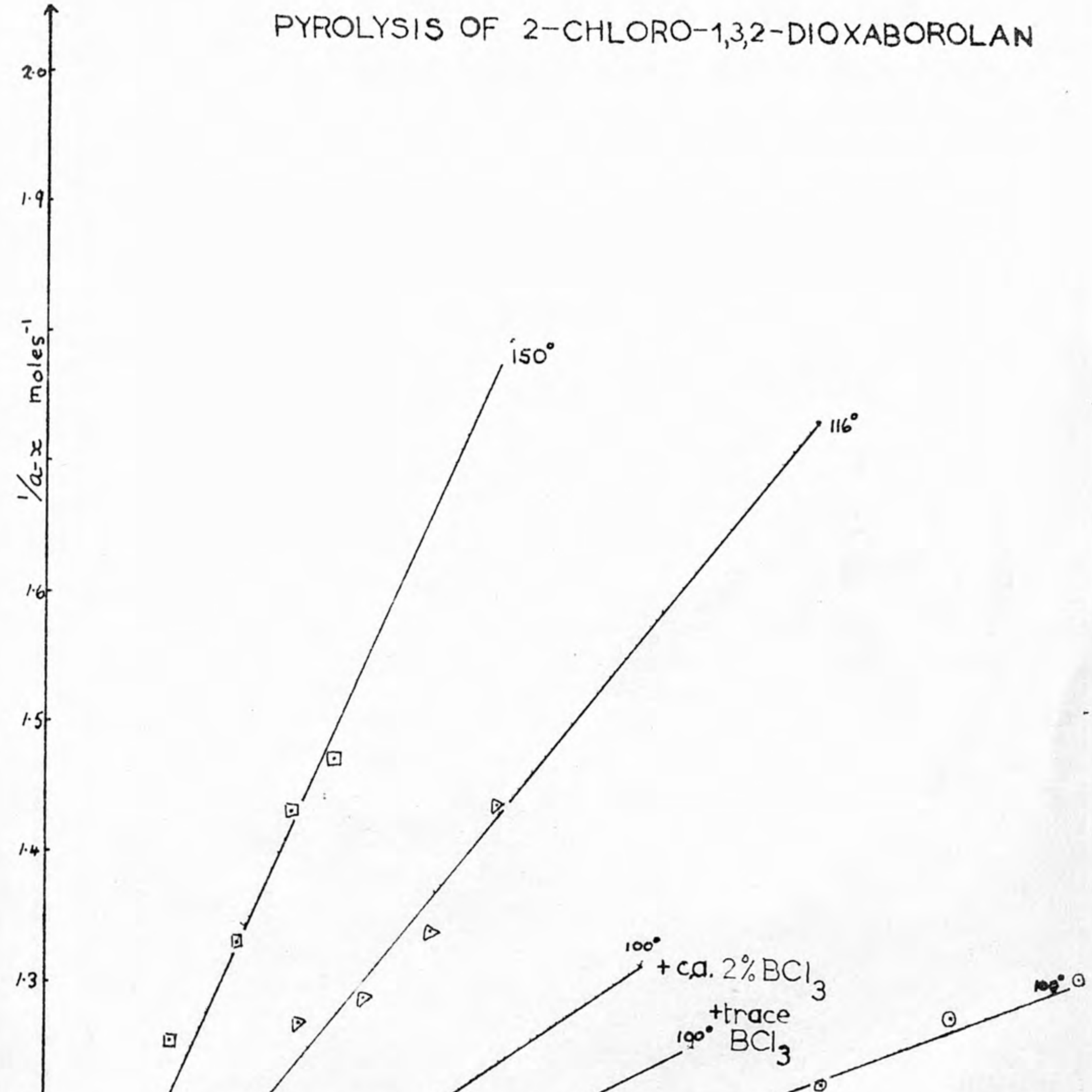


fig.8.



PYROLYSIS OF 2-CHLORO-1,3,2-DIOXABOROLAN

fig. 9.

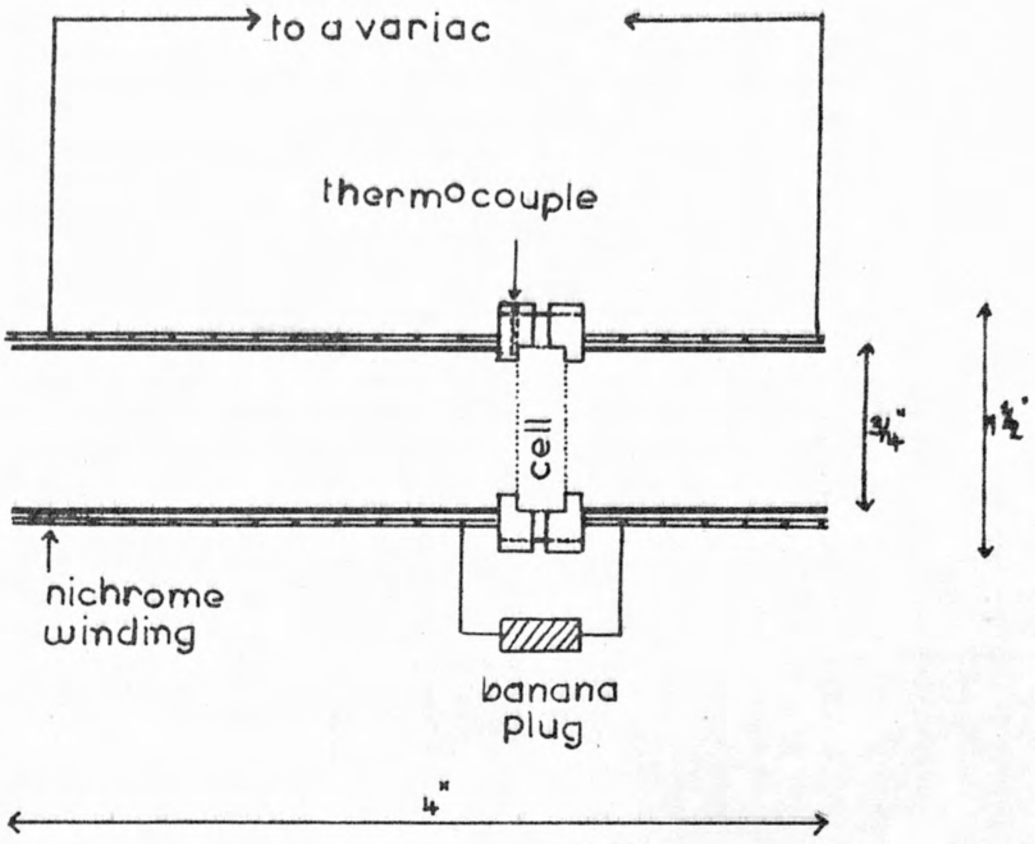

to a variac
thermocouple
cell
3/4"
1 1/2"
nichrome winding
banana plug
4"

fig.10.

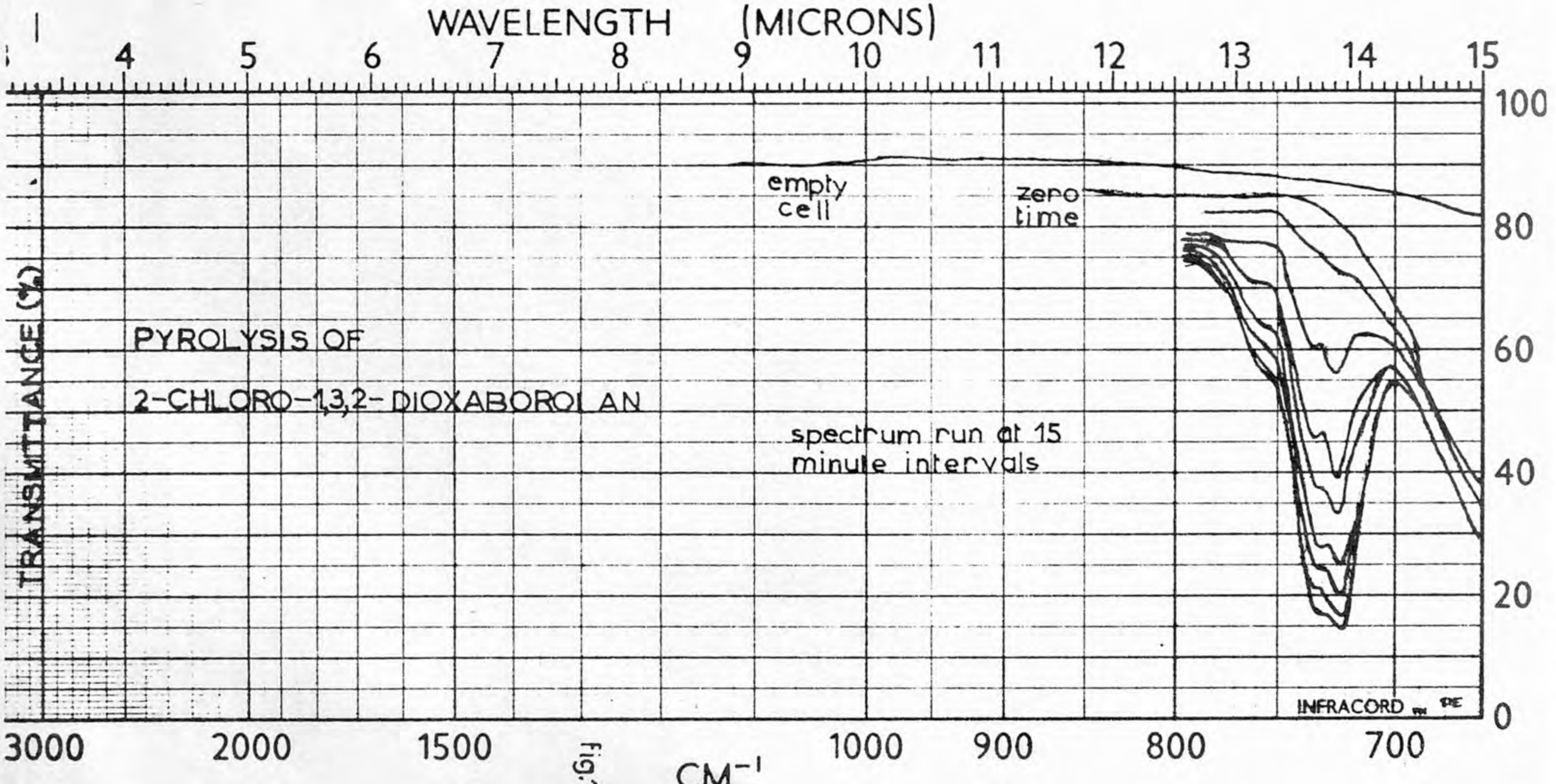
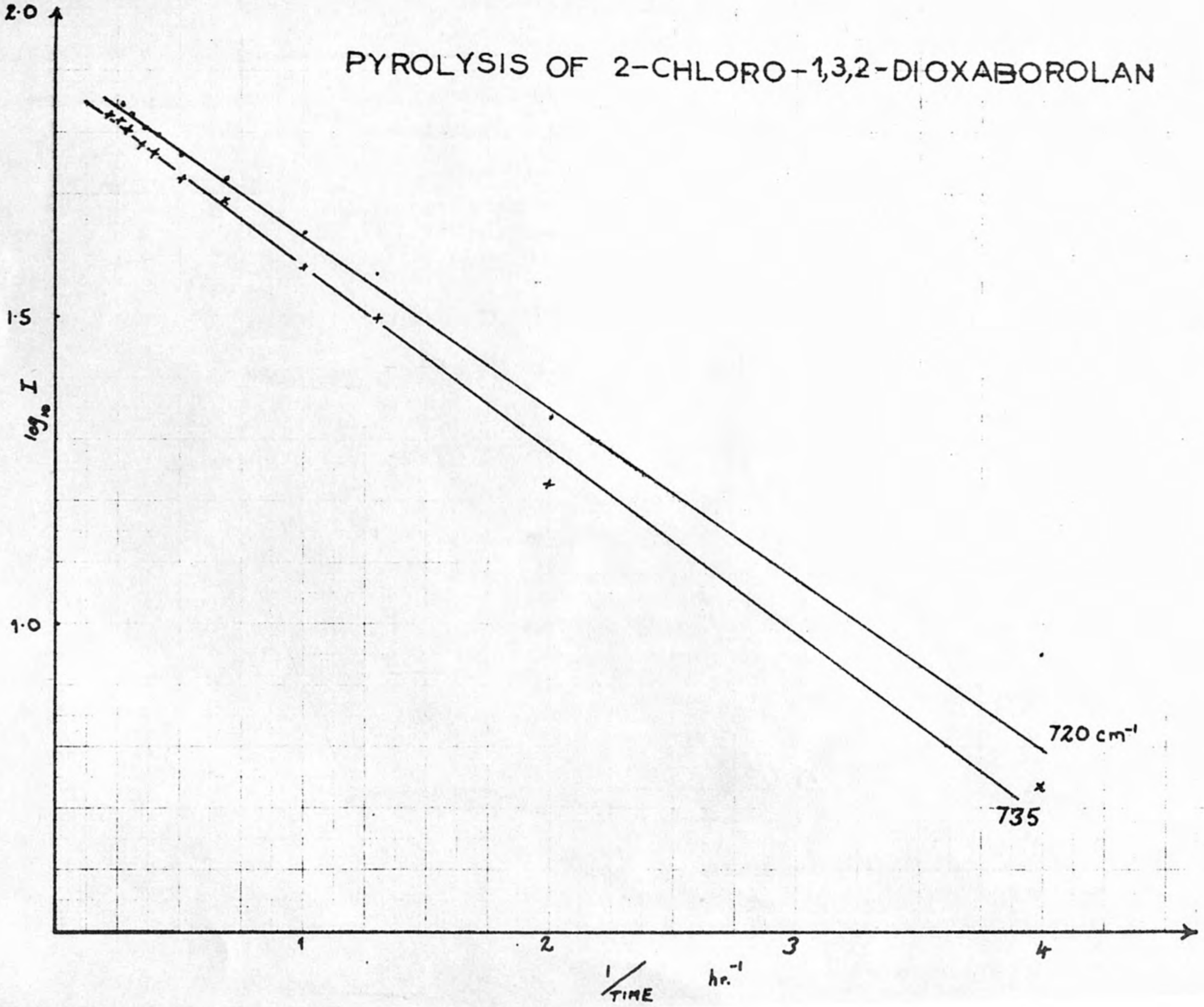

WAVELENGTH (MICRONS)
4
5
6
7
8
9
10
11
12
13
14
15
100
80
60
40
20
0
TRANSMITTANCE (%)
PYROLYSIS OF
2-CHLORO-1,3,2-DIOXABOROLAN
empty cell
zero time
spectrum run at 15 minute intervals
INFRACORD
3000
2000
1500
1000
900
800
700
CM⁻¹

Fig.11.

fig.12



PYROLYSIS OF 2-CHLORO-1,3,2-DIOXABOROLAN

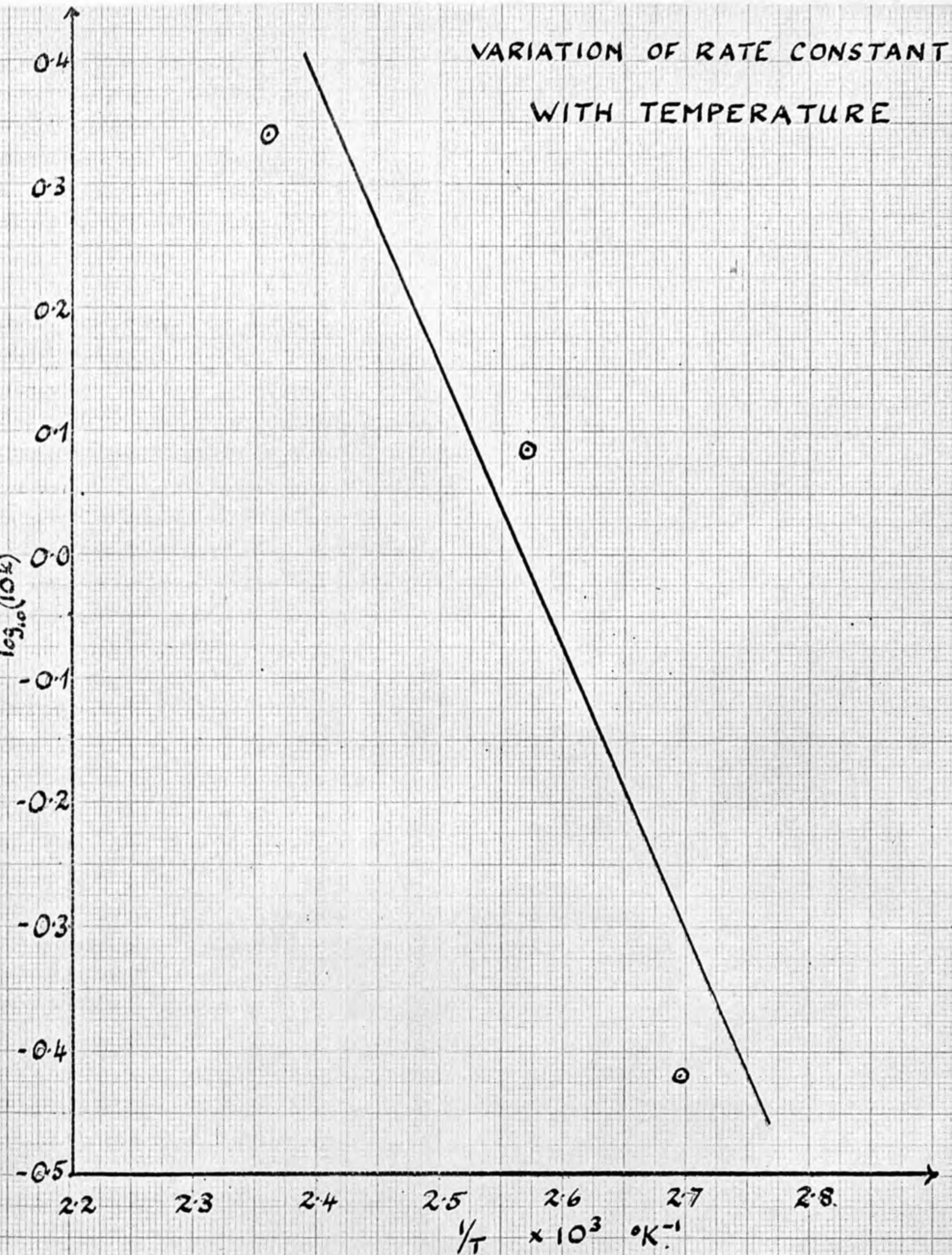
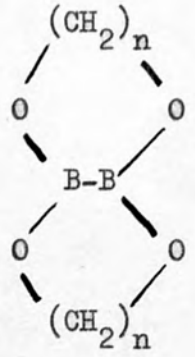

VARIATION OF RATE CONSTANT WITH TEMPERATURE

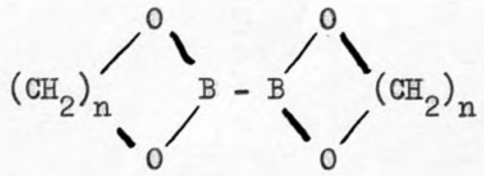
Fig. 13

Part 3: Attempted preparation of cyclic diboron compounds.

Dihydric alcohols should form two types of cyclic derivative (I and II) with diboron compounds

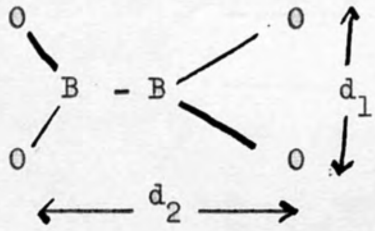


I



II

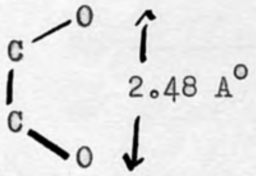
A simple calculation shows, however, that for n = 2 or 3 there will be less strain in type I

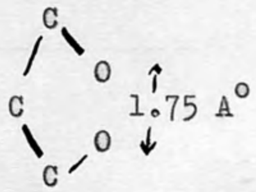


B-O 1.36 A°

B-B 1.74 A°

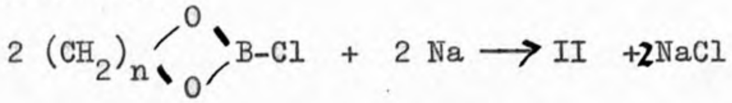
Where the B-O bond length is assumed to be close to that in H_3BO_3[53] and the B-B bond length as for B_2Cl_4[21], d_1 is calculated at 2.36 A° and d_2 3.10 A°. However, the following molecular parameters are reported for the glycols[9].





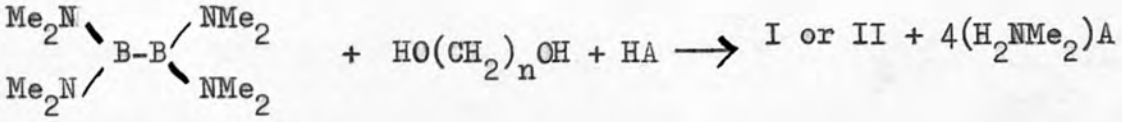
Type I is obviously even less likely for V_d symmetry

Four possible methods ofproducing such compounds were considered and are summarised below

1.


$$2\,(CH_2)_n\left<\begin{matrix}O\\O\end{matrix}\right>B\text{-}Cl + 2\,Na \longrightarrow II + 2NaCl$$

2. $B_2Cl_4 + 2\ OH(CH_2)_nOH \longrightarrow$ I or II + 4HCl

3.


$$\begin{matrix}Me_2N\\Me_2N\end{matrix}\!\!>B\text{-}B<\!\!\begin{matrix}NMe_2\\NMe_2\end{matrix} + HO(CH_2)_nOH + HA \longrightarrow \text{I or II} + 4(H_2NMe_2)A$$

Where HA is an acid.

4. $B_2(OH)_4$ (or BO) + $HO(CH_2)_nOH \longrightarrow$ I or II + $4H_2O$

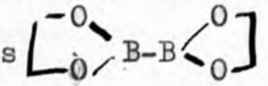
Reactions similar to these have been reported by various authors for mono functional alcohols. Wiberg et al[54] have reported the formation of a diboron compound from dimethoxychloroborane and sodium, but more recent work makes this doubtful.[55,56] Schlesinger et al have observed reactions between alcohols and B_2Cl_4,[3] and Brotherton et al have studied the alcoholysis of tetrakis (dimethylamino) diboron.[55] Holliday and Massey[7] mention the solubility of hypoboric acid in alcohols but do not go into detail. If I or II is insoluble in polar solvents reaction 4 should occur on simple mixing.

A previous attempt to prepare the cyclic derivative where n=3, from 2-chloro-1,3,2-dioxaborinan and an alkali metal was unsuccessful,[14] but this was probably the result of the extremely powerful reducing agent employed (Na/K alloy), which produced further degradation. When the alloy was replaced by a suspension of lithium particles there was no reaction. Nöth et al[56] have carried out reactions of this type with the acyclic compounds,

$(CH_3O)_2$ BCl, $(nC_3H_7O)_2BCl$, $(CH_3)_2N\ _2BCl$, and $\left[(C_2H_5)_2N\right]_2BCl$. They found that sodium reacted only very slowly, but Na/K alloy was fast and the reaction strongly exothermic for the alkoxy derivatives. In fact for these latter only small quantities of the corresponding diboron compound were isolated. This is not surprising in view of the readiness with which the alloy will attack C-O bonds in ethers.[57]

After consideration of these points it was decided to use sodium as the dehalogenating agent but to increase the rate of reaction by using a fine dispersion of the metal in toluene. If successful this would provide an unequivocable method for differentiating between types I and II.

i) The entire process was carried out in an atmosphere of dry nitrogen to prevent oxidation and hydrolysis, and all materials used were carefully dried and purified before use. The sodium dispersion was prepared by dissolving the metal in liquid ammonia, adding toluene and then allowing the mixture to warm up to room temperature with constant stirring. 2-chloro-1,3,2-dioxaborolan reacted immediately with the dispersion to produce a grey precipitate. The precipitate contained a little sodium but after filtering the solid off the remaining toluene was shown to contain a small quantity of dissolved solid, which was air sensitive. The presence of boron in the solid was indicated by a flame test. Addition of aqueous methanol followed by methyl-red indicator showed no trace of the strong acid one would expect from the hydrolysis of B-Cl linkages.

A sodium fusion confirmed the presence of boron and the absence of chlorine and nitrogen. It would therefore appear that the reaction was successful in cleaving the B-Cl bond, but only 9.6% of boron was found whereas  requires 15.3%. The first analysis, a simple caustic soda mannitol titration was thought to be at fault and so the analysis was repeated but this time the substance was treated with methanolic nitric to produce complete oxidation and the trimethyl borate distilled into a flask of water. Titration of the boron with caustic soda in the presence of mannitol was then performed. The result was only 1% lower in boron.

When the substance was deformed in a pestle and mortar it did not break up, but behaved like a plastic, gradually shaping into a thin flat disc. On warming in a sealed tube it began to soften at 90° but did not finally liquify until 134°.

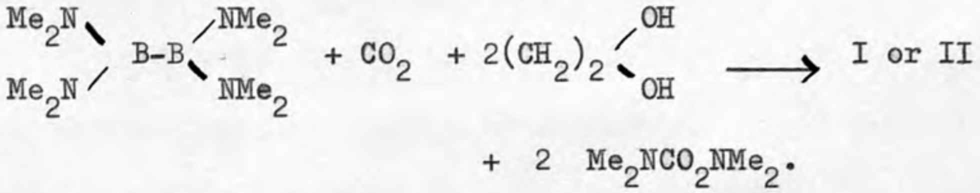
It is difficult to explain these facts other than by assuming that during the reaction some carbon oxygen bonds were broken and a polymer produced. This method was not pursued further.

ii) Reactions involving B_2Cl_4 must be carried out in vacuum and at fairly low temperatures. The diboron tetrachloride was prepared by the method of Schlesinger[3] and will be described in more detail later. In this experiment the alcohol used was propane 1,3 diol for, by comparison with 2-chloro-1,3,2-dioxaborinan one might expect the corresponding diboron compound to be a liquid and probably volatile and thus it would be amenable to vacuum purification and general handling. Purified B_2Cl_4 was condensed onto a slight excess of the glycol dispersed in carbon tetrachloride. On warming to room temperature reaction took place and a white precipitate separated out and a gas was given off. The gas, identified as HCl by its vapour pressure, was 90% of that expected from reaction 2. The very small quantity of solid obtained was sensitive to air and only handled with difficulty but it appeared to be soluble in benzene and showed the presence of boron on sodium fusion. To have continued the investigation of this substance would have required much larger quantities of B_2Cl_4 and since this compound was only available in small quantities it was decided to await the preparation of the cyclic diboron compound by some other method and then compare the properties with a fresh sample obtained by this method.

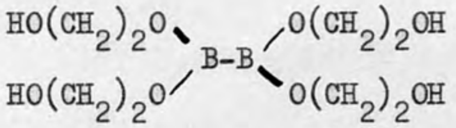
iii) Before attempting reaction 3 the method of separating the products was considered. The most useful acid is HCl since it is strong and will not oxidise the B-B bond. Therefore one product in the reaction will be dimethylammonium chloride. In order to separate this compound from the expected solid diboron compound ten solvents were tried, but only one, chloroform, was found to be useful.

The reaction between $B_2[N(CH_3)_2]_4$, ethylene glycol and HCl was performed in ether under an atmosphere of dry nitrogen. The reaction was exothermic but required an induction period of c.a. two hours. The reaction products were filtered off and treated with chloroform, but all dissolved. Benzene did not remove any of the diboron compound and vacuum sublimation did not afford a separation either. It was possible however to show the presence of a diboron compound in the mixture since it yielded hydrogen when mixed with dilute caustic soda and reduced ammoniacol silver nitrate to silver.

In a second attempt to utilise the ammino diboron compound it was decided to try CO_2 as the acid. This time however one of the products expected is dimethylamino dimethylcarbamate.



The reaction was again carried out in ether and again had an induction period though this time only half an hour. When it occurred the reaction was sudden and highly exothermic precipitating a dense white solid. After filtering off the solid it was sublimed in vacuum and then analysed for boron. Four boron determinations were carried out first by the normal mannitol caustic soda titration and then by the methanolic nitric acid method described previously. The results varied from 8.4 to 4.4% indicating a non-homogeneous product. It is perhaps worth noting that the compound



contains 8.4% boron. The presence of boron-boron bonds was shown as before

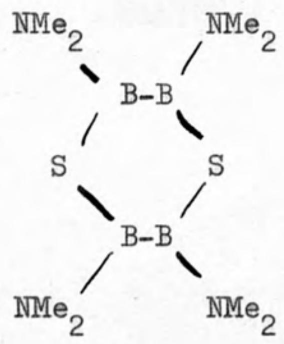
An oily liquid obtained from the ether was identified as dimethylamino dimethylcarbamate by comparison of its properties with those of an independently prepared sample.

It was unfortunate that this method was unsuccessful because of the ease with which the carbamate can be separated from the solid products. It is possible that if the reaction was carried out at lower temperatures it would proceed as expected or perhaps in more dilute solutions the reaction would be more controllable.

iv) The reaction between tetrahydroxydiboron and glycols was not studied in detail. It was noted that $B_2(OH)_4$ was soluble in ethylene glycol, but on standing the mixture in a vacuum desiccator over P_2O_5 for two weeks to remove the water formed in the reaction, no precipitate was obtained though the solution was still as strongly reducing towards silver nitrate as before. It is possible that the cyclic diboron compound was formed but was soluble in the glycol or that the solution was just a simple mixture.

It was concluded from these experiments that some diboron compounds were in certain instances obtained but that there was no evidence for them being cyclic, and some were probably polymeric in nature. It would be of interest to study reaction 3 in more detail and perhaps thereby to separate the reaction product into its individual components.

Just recently a six membered ring containing B-B bonds has been prepared from tetrakis (dimethylamino) diboron and HCl and H_2S[58].



Its structure has been confirmed by molecular weight and boron n.m.r. measurements.

SECTION B.

Part 1: Theoretical Considerations in Spectroscopy.

i) Introduction.

In the past two decades and particularly since the innovation of computers, theoretical infra-red spectroscopy has undergone considerable progress. No longer are our calculations confined to the simplest of molecules and in a later section the vibrational problem for a ten atom molecule is discussed in some detail.

Numerous authors[59-61] have dealt with this topic in more detail than will be presented presently, however it was thought desirable to give a brief survey of the methods which will be used in later chapters.

ii) Setting up the Problem.

If the molecule is pictured as a set of point masses connected by springs it is possible to express the kinetic (T) and Potential (V) energy of the molecule in terms of the geometry of the molecule the atomic masses and the "strength" of the spring or force constant f.

The potential energy is easily expressed in the harmonic approximation in terms of the intermolecular displacements by using Hooke's Law

$$2V = \sum_{i,j}^{3N-6} f_{ij} q_i q_j$$

where q_i is the i^{th} displacement

In matrix notation

$$2V = R' F R$$

Where R is a column matrix expressed in terms of the q's and R' is its transpose.

$$R = \begin{bmatrix} q_1 \\ q_2 \\ q_{3N-6} \end{bmatrix}$$

and $F = \begin{vmatrix} f_{11} \; f_{12} \cdots\cdots f_{1,3N-6} \\ \\ f_{3N-6,1} \cdots\cdots f_{3N-6,3N-6} \end{vmatrix}$ or, as it is sometimes written $\begin{vmatrix} F_{11} \cdots\cdots F_{1,3N-6} \\ \\ F_{3N-6,1} \cdots F_{3N-6,3N-6} \end{vmatrix}$

Wilson[60] has shown how the kinetic energy may also be expressed in terms of the internal co-ordinates R

$$2T = \dot{R}' G^{-1} \dot{R}$$

where $\dot{R} = \frac{d}{dt}(R)$ and G is the kinetic energy matrix defined by

$$G_{ij} = \sum_k \frac{B_{ik} B_{jk}}{M_k}$$

M_k is the mass of atom k and $\frac{1}{M_k} = \mu_k$

The B_{ik} are expressions involving the geometry of the molecule

$$B_{ik} = \frac{\partial R_i}{\partial \xi_k}$$ the ξ_k referring to some co-ordinate axis ξ_k

In matrix notation $G = BM^{-1}B'$, M is a diagonal matrix involving the atomic masses μ_k

It is often more useful to express G in a slightly different form by putting $D = BM^{-\frac{1}{2}}$. Then $G = DD'$

Substitution for V and T in Lagrange's equation

$$\frac{d}{dt}\left(\frac{\partial T}{\partial \dot{q}_k}\right) - \frac{\partial V}{\partial q_k} = 0$$

and assuming a harmonic relationship $R_k = A_k \text{ Cos } 2\pi\nu t$ where ν is a fundamental frequency, then it may be shown that for a non-trivial solution for the constants A_k

$$\begin{vmatrix} F_{11} - (G^{-1})_{11} & \cdots\cdots & F_{1\ 3N-6}(G^{-1})_{1\ 3N-6} \\ F_{21} - (G^{-1})_{21} & & \vdots \\ \vdots & & \vdots \\ \cdots & \cdots & \cdots \end{vmatrix} = 0$$

With $\lambda^{\frac{1}{2}} = 2\pi\nu$

In matrix notation $F - G^{-1}\Lambda = 0$, or $GF - \Lambda = 0$

The solution of this equation will be discussed later.

It was not intended to give more than a brief synopsis of the method for obtaining this equation, but this has served the purpose of introducing some useful relationships. ~~Except~~ Where necessary this is the procedure which will be used in future.

iii) General Techniques for finding the G matrix elements.

G_{ij} was defined in terms of B_{ik} or $\frac{\partial R_i}{\partial \xi_k}$. Hence it is only necessary to express the internal displacement co-ordinates R in terms of their cartesian counterparts and differentiate with respect to one axis at a time. For a molecule with N atoms there will be 3N-6 internal co-ordinates R (3N-5 for a linear one) each of which must be expressed in the ξ_i. This method is not elegant and can be tedious, but when computers are available for solving the secular equation this is the usual procedure (c.f. later).

An internal co-ordinate R_t can be expressed in terms of ξ_i by:-

$$R_t = \sum_{i=1}^{3N} B_{ti}\,\xi_i \qquad t = 1, \ldots\ldots\ldots\ldots 3N-6$$

i refers to co-ordinate ξ_i

The B_{ti} may be considered as the components of a vector $s_{t\alpha}$ and the ξ_i as components of a vector ρ_α all associated with atom α

Now $$R_t = \sum_{\alpha=1}^{N} s_{t\alpha} \cdot \rho_\alpha$$ using standard vector notation

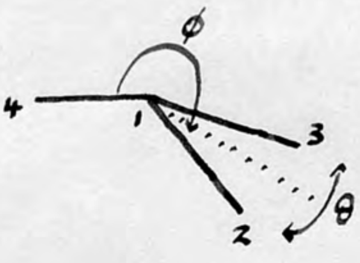
The problem has now been reduced from 3N to N. $s_{t\alpha}$ is in that direction which produces a maximum change in R_t for all $s_{t\beta} = 0$ and of a magnitude equal to the change in R_t produced by a unit displacement of atom α in this direction. It is usual to express the $s_{t\alpha}$ in terms of unit vectors e along the bonds. e_{21} is a unit vector from atom 2 to atom 1.

Substituting for the B_{ti} in $G_{tt'}$ gives

$$G_{tt'} = \sum_{\alpha=1}^{N} \mu_\alpha\, s_{t\alpha} \cdot s_{t'\alpha}$$

t and t' refers to internal co-ordinates R_t and $R_{t'}$.

When the problem was to be set up in the 'B' matrix form for solution by a computer there would sometimes be difficulty in obtaining the necessary geometrical relationships in three dimensions. The following extension of the s vector technique shows how this may be overcome. For simplicity the method is presented in the form of an example



$$r_{12} = r_{13} \neq r_{14}$$

Let $R_t = r_{14}\Delta\phi$ with atom 4 not lying in the 1,2,3 plane at equilibrium and the Y axis bisecting 2 1 3.

$$s_{t3} = \frac{-e_{12} \times e_{13}}{r_{13}/r_{14} \text{ Sin } \theta} \qquad \text{(cross product)}$$

Similarly for s_{t2} atoms 1 and 4 lie along the Y axis and so the B matrix entries are obvious.

But $\quad s_{t3} = (\underline{i}\ B_{tx} + \underline{j}\ B_{ty} + \underline{k}\ B_{tz})$

Where $\underline{i}$, $\underline{j}$, $\underline{k}$ are unit vectors along x, y, z.

Since $\underline{i} \cdot \underline{i} = 1$ and $\underline{i} \cdot \underline{j} = 0$ etc. then $s_{t3} \cdot \underline{i} = B_{tx} = \dfrac{-e_{12} \times e_{13}}{r_{13}/r_{14} \text{ Sin } \theta} \cdot \underline{i}$

The e vectors may always be expressed in the form

$$e_{12} = a_{12}\underline{i} + b_{12}\underline{j} + c_{12}\underline{k} \text{ etc.}$$

a, b, c are defined by $e_{12} \cdot \underline{i} = a_{12}$ etc. and $e_{12} \cdot e_{12} = a_{12}^2 + b_{12}^2 + c_{12}^2 = 1$ etc.

Here $e_{12} = \text{Sin } \theta\ \underline{i} - \text{Cos } \phi \text{ Cos } \theta\ \underline{j} - \text{Sin } \phi \text{ Cos } \theta\ \underline{k}$

A similar relationship is obtained for e_{13}. If the product $e_{12} \times e_{13}$ is obtained and then dotted with $\underline{i}$ the 'B' terms are obtained. In some cases this method will be slower than direct observation but it does provide a useful check, and for molecules with a complicated geometry it may prove propitious. When the G matrix was required directly, the vector method was always used.

iv) Application of Symmetry Properties.

It is impossible to give more than a very brief description of the basis and methods involved.

As previously constructed the G and F matrix have dimensions (3N-6) by (3N-6) for an N atom molecule. For molecules containing four or more atoms the solution of the secular equation on a hand calculator will be very long and tedious. If full use of the molecular symmetry is made the problem can often be reduced to a number of smaller ones. The secular equation is then said to be factored.

It is physically obvious that a problem can be set up in any coordinates and yet still have the same solution in terms of the λ_i (the eigenvalues).

If G is set up in some co-ordinate 'q' then it should be possible to transform G into G^+ where G^+ is in terms of an equivalent set of co-ordinates q^+. Let this transformation be expressed in matrix notation by U such that:-

$$\left[q^+\right] = U \left[q\right]$$

If U is correctly chosen then some of the off diagonal terms in G^+ will be zero. As an example

$$\begin{bmatrix} G_{11} & G_{12} & G_{13} & G_{14} & \cdots & G_{1n} \\ G_{21} & \cdots & & & \cdots & G_{2n} \\ \vdots & & & & & \vdots \\ G_{n1} & \cdots & & & \cdots & G_{nn} \end{bmatrix} \qquad n = 3N-6$$

and

$$\begin{bmatrix}
G_{11} & G_{12} \cdots & G_{1r} & 0 & 0 & 0 & 0 \cdots\cdots & 0 \\
G_{21} & & \vdots & 0 & 0 & \cdots\cdots & & 0 \\
\vdots & & \vdots & \vdots & & & & \vdots \\
G_{r1} & \cdots\cdots & G_{rr} & 0 & \cdots\cdots & & & 0 \\
0 & 0 \cdots\cdots & 0 & G_{ss} & \cdots & G_{st} & 0 \; 0 \cdots\cdots & 0 \\
\vdots & & \vdots & \vdots & & \vdots & \vdots & \vdots \\
0 & \cdots\cdots & 0 & G_{ts} & \cdots & G_{tt} & 0 \cdots\cdots & 0 \\
0 & \cdots\cdots & & 0 & \underline{\qquad\qquad} & & 0 \cdots\cdots & 0 \\
0 & & & \vdots & & & \vdots & \vdots \\
0 & & & \vdots & & & \vdots & \vdots \\
\vdots & & & \vdots & & & \vdots & \vdots \\
0 & \cdots\cdots & & 0 & \underline{\qquad\qquad} & & 0 \cdots\cdots & 0
\end{bmatrix}$$

$s = r + 1$

the shaded block also has non zero elements

Here the problem has been shown to factorise into three smaller ones. A similar situation arises for the force constant matrix. This is equivalent to saying that the potential and kinetic energy contains no cross terms such as G^+_{rs}, F^+_{rs} when expressed in terms of the q^+ and r and s refer to different blocks.

When the co-ordinates q^+ obey the same transformation as the symmetry properties of the molecule they are called symmetry co-ordinates.

G and F were transformed into symmetry co-ordinates (usually denoted S) as follows:-

$$\mathcal{G} = UGU' \qquad \mathcal{F} = UFU'$$

where the $\mathcal{G}$ and $\mathcal{F}$ are expressed in terms of symmetry co-ordinates.

The terms in U were either found by inspection or by application of the following formula

$$S^{\gamma} = N \sum_{p} \chi^{\gamma} \quad (PR_1)$$

where N is a normalisation constant and S^{γ} is the symmetry co-ordinate belonging to the class γ of the total point group, H say, to which the molecule belongs. χ^{γ} represent the character under the symmetry operation P in class γ and R_1 represents some internal co-ordinate. (PR_1) is used to represent the co-ordinate into which R_1 is sent by operation P. The sum is only taken over all the group operations required to generate all the R_i.

It is not possible to go into the group theory used in more detail without reproducing large sections of available texts.[59,60]

v) Normal Co-ordinates.

The normal co-ordinates Q_k are related to the symmetry co-ordinates S by the following relationship, where matrix notation is again used.

$$S = \mathcal{L}Q$$

Substituting for S in the potential and kinetic energy

$$2T = \dot{S}'G\dot{S} \quad \text{and} \quad 2V = S'FS$$

followed by the previous use of Lagranges equation for obtaining the secular equation gives:-

$$(\mathcal{G}\mathcal{F} - \Lambda)\mathcal{L} = 0$$ or if Q is definted in terms of internal co-ordinates

$$R = LQ \quad \text{and} \quad (GF - \Lambda)\,L = 0$$

Furthermore, it can be shown that $G = LL'$, $\mathcal{G} = \mathcal{L}\mathcal{L}'$ and $\mathcal{L}'\mathcal{F}\mathcal{L} = \Lambda$ $L'FL = \Lambda$

In order to produce a diagramatic representation of the normal co-ordinates they were required in cartesian form. The following equations summarise the method.

If $R = BX$ where X is the matrix of cartesian displacements corresponding to R_1, R_2 .... R_{3N-6} and $S = UR$ then $S = UBX$

Hence $X = B^{-1}U'LQ$ (N.B. $U^{-1} = U'$)

But B^{-1} may be found from kinetic energy requirements to give

$$X = M^{-1}B'U'\mathcal{G}^{-1}\mathcal{L} \quad ; \quad \text{since } \mathcal{G}^{-1} = (\mathcal{L}\mathcal{L}')^{-1} = \mathcal{L}\mathcal{L}^{-1}$$
$$X = M^{-1}B'U'\mathcal{L}Q$$

All the matrices are known or easily determined.

vi) <u>Determination of eigenvalues and eigenvectors on a hand calculating machine.</u>

When the GF matrix was of dimensions 3 x 3 or less it was easy to solve for the eigenvalues and eigenvectors on a hand calculating machine. The method employed is an iterative one and was first suggested by Long and Thomas[67].

An arbitrary column matrix of n entries was chosen and pre-multiplied by $\mathcal{G}\mathcal{F}$, where $\mathcal{G}\mathcal{F}$ has dimensions n x n. Let the vector be $\bar{l}_1$. The resulting column was then scaled down so that one member was unity. The new vector $\bar{l}_2$ was then used to generate $\bar{l}_3$ by the same process. This procedure was continued until $\bar{l}_m = \bar{l}_{m-1}$. The final scalar factor is λ_1, and $\bar{l}_m$ the unnormalised modul column. To obtain λ_2, $\mathcal{G}\mathcal{F}$ was reduced by post-multiplication by a reducing matrix w where

$$w = \begin{vmatrix} 0 & -\alpha^{-1}\beta \\ 0 & I \end{vmatrix} \qquad \text{I is the unit matrix}$$

For the general case where p roots and vectors are known, α and β are found by assembling the modul rows using $\mathcal{L}_p^{\prime} \mathcal{F}_p = \mathcal{L}_p^{-1}$ into a matrix of p rows and n columns and partitioning it into two matrices of α and β where α has dimensions p x p and β px(n-p). λ_{p+1} was found by repeating the iteration. The $\bar{l}_p$ were normalised by using the equation

$$N_p^2 \ \bar{l}_p^{\prime} \ F \ \bar{l}_p = \lambda_p$$

where N is the normalising factor. The results were checked as follows:-

a) For orthogenality, $\bar{l}_p \ \bar{l}_q = 0$ and $\bar{l}_p \ \bar{l}_p^{-1} = 1$

b) ~~$l_p l_p$ pp~~ $l_p l_p^{\prime} = \mathcal{G}_{pp}$

c) The sum of the roots is equivalent to the trace of the $\mathcal{G}\mathcal{F}$ matrix.

vii) Computer Techniques.

Certain problems were set up in 'B' matrix form for solution on a computer. The data was fed into the machine as B matrix, M matrix and F matrix. The program was constructed so that the B matrix was first stored and $M^{-\frac{1}{2}}$ found. D was formed by multiplying B and $M^{-\frac{1}{2}}$, $D = BM^{-\frac{1}{2}}$, then $D^{\prime}FD$ obtained. The computer was then instructed to find the eigenvalues and eigenvectors of $D^{\prime}FD$ by using a library programme. Let $D^{\prime}FD$ have eigenvalues in matrix form Λ^{*} and eigenvectors Y

Then $\quad D^{\prime}FDY - Y\Lambda^{*} = 0$

Pre-multiplication by D gives $DD^{\prime}FDY - DY\Lambda^{*} = 0$

$$= GFDY - DY\Lambda^{*}$$

But GF has a unique set of eigenvalues Λ and eigenvectors L. Hence $DY = L$ and $\Lambda^{*} = \Lambda$

In one problem it was necessary to find $\mathcal{G}$ first by vector techniques and then $\mathcal{F}$. The computer then multiplied them together and solved as before. The reasons for this are given in the section on dimethylamine.

It should be noted that although B has dimensions 3N-6 x 3N and therefore includes redundant co-ordinates DD' has dimensions (3N-6) x (3N-6) and consequently redundant co-ordinates have been removed.

Actual programs were designed for the London University Atlas computer.

viii) Band Shapes.

For linear and diatomic molecules in the gas phase the infra-red absorptions corresponding to dipole changes perpendicular to the molecular axis contain a strong central peak called the Q branch. When the vibration occurs parallel to this axis the Q branch is forbidden. For symmetric or asymmetric top molecules the situation is more complicated. Vibrations are now described according to whether they induce dipole changes parallel to the least, most or intermediate moment of inertia. The usual convention is that the moment of inertia I_C refers to the greatest and I_A the least, and type A bands are those in which the vibration is parallel to I_A.

The band shapes for asymmetric rotors have been discussed in detail by Badger and Zumwalt[63]. For symmetric rotors Gerhard and Dennison[64] have shown how to obtain the separation $\Delta\nu$ between the maxima of the P and R branches and the general appearance of the band when the individual rotational lines are unresolved. They define a constant β where

$$\beta = I_A/I_C - 1$$

and $\Delta \nu = S(\beta)\left[(kT/I_A)^{\frac{1}{2}}/\pi\right]$ for parallel vibrations

with $\log_{10} S = 0.721/(\beta + 4)^{1.13}$

k is the Boltzman constant.

For these vibrations the ratio $R = \frac{I_o}{L}$ for the Q branch intensity I_o to the intensity of the complete band L was plotted as a function of β.

The band shapes for perpendicular vibrations are given for various values of β combined with an estimate of the P R separation.

Hence, if the moments of inertia for a particular symmetric rotor molecular are known or can be estimated it is possible to determine the expected band shapes.

ix) Intensity.

The intensity of infra-red bands has been reviewed in detail by various authors.[31,65,66] It is customary to define the intensity Γ by

$$\Gamma = \frac{1}{cl} \int \ln\left[(I_o)_\nu / (I)_\nu\right] \, d \ln \nu$$

where l is the path length, c the concentration of absorbing material and $(I_o)_\nu$ and $(I)_\nu$ the initial and final intensity of a beam of frequency ν cm.$^{-1}$ Γ is related to the dipole moment derivative $\frac{\partial \mu}{\partial Q_i}$ as follows:-

$$\Gamma_i = \frac{1}{\nu_i} \frac{N\pi}{3C} \left(\frac{\partial \mu}{\partial Q_i}\right)^2$$

for normal co-ordinate Q_i N is the number of moles per ml. and C the velocity of light.

Although this formula can be used easily it does not give a good pictorial representation. If it is assumed that on stretching a bond by dr a change of dipole moment is produced equal to $\left(\frac{\partial\mu}{\partial r}\right)$ dr along the bond and that for angle changes the corresponding change is $\left(\frac{\partial\mu}{\partial\theta}\right)$ dθ perpendicular to the band and in the plane of movement, then it is possible to visualise the overall dipole moment change in terms of bond localised ones.

The following method was used in a later section to obtain $\left(\frac{\partial\mu}{\partial Q}\right)$ when $\left(\frac{\partial\mu}{\partial r}\right)$ and $\left(\frac{\partial\mu}{\partial\theta}\right)$ were assumed from a knowledge of other molecules.

Write $\mu = \sum_{\beta}\mu_{\beta}$ where β refers to bond β

Expressing μ in terms of its components along cartesian co-ordinates ξ_i then:-

$$\mu_{\xi_i} = \sum \mu_{\beta}\, m_{\beta\xi_i}$$

where $m_{\beta\xi_i}$ is the direction cosine of μ_{β} on ξ_i

Now $$\frac{\partial\mu_{\xi_i}}{\partial S_j} = \sum_k \frac{\partial\mu_{\xi_i}}{\partial R_k}\;\frac{\partial R_k}{\partial S_j}$$

with the summation going over all the internal co-ordinates R_k contributing to S_j.

The second term in the summation is $(U^{-1})_{kj}$.

N.B. U^{-1} will not exist unless U is made square by including all the redundancies, however U will be orthogenal and hence $U^{-1} = U'$. For the redundancies therefore the summation over the redundant co-ordinates will be zero. Thus:-

$$\frac{\partial\mu_{\xi_i}}{\partial S_j} = \sum_k \frac{\partial\mu_{\xi_i}}{\partial R_k}\; U'_{jk}$$

The U matrix has been defined previously.

To find $\frac{\partial \mu}{\partial Q}$ we note that $\frac{\partial \mu_{\xi_i}}{\partial Q_t} = \sum_{t,j} \frac{\partial \mu_{\xi_i}}{\partial S_j} \frac{\partial S_j}{\partial Q_t}$

i.e. $\frac{\partial \mu_{\xi_i}}{\partial Q_t} = \sum l_{t,j} \frac{\partial \mu_{\xi_i}}{\partial S_j}$

Where l_{tj} is the entry in the t th row and j th column of $\mathcal{L}$ defined earlier.

Hence $$\frac{\partial \mu_{\xi_i}}{\partial Q_t} = \sum_{t,j} \sum_{k} \frac{\partial \mu_\beta}{\partial R_k} m_{\beta \xi_i} U_{jk} \, l_{t,j}$$

and $$\frac{\partial \mu}{\partial Q} = \sum_{i} \frac{\partial \mu_{\xi_i}}{\partial Q_t}$$

x) <u>Selection Rules</u>

Fundamental transitions occur from states with vibrational quantum number v = 0 to v = 1 only if one of the integrals

$$\int \Psi_0 (Q_i) \mu_{\xi_i} \Psi_1 (Q_i) d\tau \text{ ....(1)}$$

(where ξ_i = x, y, z) are non zero. Ψ_v are the wave functions and τ is an element of space. For a harmonic oscillator the Ψ_v are proportional to the product of an exponential function of the normal co-ordinate Q_i and absorption frequency ν, and Hermite functions H

$$\Psi_v = N e^{-\frac{1}{2}\gamma Q_i^2} H_v (\gamma^{\frac{1}{2}} Q_i)$$

N is a constant and $\gamma = \frac{4\pi^2 \nu_k}{h}$

Now $H_o = 1$ and $H_1 = 2\gamma^{\frac{1}{2}} Q_i$.

Thus the symmetry of the Ψ_1 with respect to symmetry operations will depend upon the symmetry of Q_i though Ψ_o will behave as though it were of a totally symmetric species.

Now it can be shown[59] that equation (1) will only be non zero if the complete integral remains the same after any symmetry operation. If equation (1) goes to minus equation (1) then the integral will evaluate to zero. This can only occur if the product $\Gamma_{Qi} \Gamma_{\xi i}$ belongs to the totally symmetric species of the molecular point group. Γ_{Qi} represents the symmetry species for Q_i and $\Gamma_{\xi i}$ the species for a translation along the ξ_i co-ordinate axis. For brevity this latter requirement only is stated.

It is not possible to discuss the determination of Γ_{Qi} or $\Gamma_{\xi i}$ in more detail however. Suffice it to say that if Γ_{Qi} and $\Gamma_{\xi i}$ are found to belong to the same symmetry species, then the fundamental transition is allowed. Where necessary the group character tables have been given and the $\Gamma_{\xi i}$ included.

Part 2: The infra-red Spectrum of B_2F_4.

Introduction.

It was mentioned previously that diboron tetrachloride (B_2Cl_4) has been studied in the gas liquid and phases by various physical techniques and that the compound possessed V_h symmetry in the solid state but V_d in the liquid and gas phase. Low temperature calorimetry[68] and infra-red[19] studies have placed the energy barrier to rotation about the B-B bond between 1 · 5 and 1 · 7 k cals. mole^{-1}. A comparison of the structure of the diboron compounds was, therefore, desirable in order to ascertain how the structure varies with the substituents.

Technique.

The preparation of B_2F_4 is discussed in a later chapter. Spectra were recorded on a Unicam SP100 from 400 to 3500 cm.$^{-1}$, and below 400 cm.$^{-1}$ on a far infra-red grating spectrometer constructed in this laboratory and described elsewhere[69]. 10 cm. path length gas cells were used with KBr or rigidex polythene windows as required and cemented on with secotine glue. Pressures were varied from a few mm. of Hg upwards. The observed spectra are shown in figures 14 and 15, and the corresponding frequencies are listed in table 6. It was apparent from these that traces of BF_3 were present in the samples and that the amount increased slowly with time.

When this work was completed a private communication was received from Gayles and Self of Oregon State University who were kind enough to offer information of their work on this compound. They prepared the compound, by the method of Brotherton et al[70], from boron monoxide and SF_4. Several weak to moderate bands listed in Table 5 were not observed by these workers indicating the greater purity of their sample, but apart from these the two sets of data are in good agreement. They conclude, from an examination of band shapes and P, Q, R separations, that the molecule has V_d symmetry, as opposed to V_h or V. Free rotation about the B-B is discussed briefly but is not favoured since CH_2FBF_2[71] is believed to possess a significant potential barrier. Since the available evidence was by no means conclusive it was decided to supplement the calculations already carried out with an estimation of relative intensities and if possible to find some method for treating the problems of symmetry and allowed transitions for a free rotor.

The three possible structures for B_2F_4 then, were:-

i) A planarmolecule with the angle τ between the two BF_2 planes, zero. Symmetry V_h

ii) BF_2 planes staggered ($\tau = 90°$). Symmetry V_d.

iii) Free rotation about the B-B bond.

By comparison with B_2Cl_4 and since the modes described as E for V_d symmetry are not split the intermediate value for τ is ruled out.

Case iii) corresponds to an energy barrier less than kT whereas for ii) it would be much greater. The problem of finding a 'point" group for describing the symmetry of a freely rotating molecule will be discussed later.

In the following calculations the nomenclatur recommended by Mulliken[72] has been used. Figure 16 shows the co-ordinate axes and the symbols for geometrical parameters employed.

<u>Calculations.</u>

Crawford and Wilson have shown[73] that where a torsion or twist angle for a given molecule can be defined to be orthogonal to all other symmetry co-ordinates the vibrational problem can be solved independently of this torsion by simply dropping the appropriate row and column of the G and F matrices. In the following the torsion is ignored since the co-ordinates are readily defined to comply with this requirement.

The G matrix terms for a molecule X_2Y_4 have been tabulated by Mann and Fano[19] for the general case in which τ , the angle between the two XY_2 planes, is unspecified. Typographical errors occur in G 9, 11 and G 10,11 which should both be of opposite signs. The force constants for the symmetry co-ordinates were determined as linear combinations of valence force constants by the matrix transformation.

$$\mathcal{F} = UFU'$$

where $\mathcal{F}$ is the symmetrical force constant matrix, F is the corresponding valence force constant matrix and U is the transformation matrix from valence to symmetry co-ordinates. The symmetry co-ordinates and the general $\mathcal{F}$ terms are listed in Table 7.

As there are no structural data on B_2F_4 in the gaseous phase, the geometrical parameters used were taken from the crystal data of Trefonas and Lipscomb.[22] Assuming a 120° B-B-F angle the bond lengths in the crystal are 1.67 Å for the B-B bond and 1.32 Å for the B-F bond.

An obvious source of values for the B-F force constants is the data of BF_3. Force constants based on this data have been evaluated by several authors.[egs. 74,75] Due to symmetry restrictions the only constants which may be determined are as given in Table 7. In deriving F for B_2F_4 it was assumed that the forces resisting deformation of the BBF angles are equal to those for the FBF angle. Since the restoring forces are principally determined by the electron configuration in the immediate vicinity of the central atom this ought to be a reasonable approximation. Likewise all interaction force constants involving α (see figure 16) are taken to be equal to their β counterparts. The numerical values assumed are given in Table 8. The only value of a B-B stretching force constant in the literature is based on a Urey Bradley force field.[19] Based on this value a valence force constant of 3.0 mdynes/Å was assumed.

The calculated frequencies of $^{11}B_2F_4$ for $\tau = 0^\circ$ and $\tau = 90^\circ$ are given in Table 9.

The force constants for BF_3 are based on the harmonic vibrational frequencies, which all lie about 5% above the observed frequencies. To obtain a reasonable comparison between the calculated frequencies of B_2F_4 and the observed it is necessary then to correct one or the other set for anharmonicity. It is reasonable to assume the same average anharmonicity for B_2F_4 as for BF_3 in which case the calculated frequencies must be reduced by 5%.

The form of the normal co-ordinates was obtained by the procedure already described and the in plane modes for V_h symmetry are shown in Figure 17. It was necessary to obtain the B matrix for the calculation and this is given in Table 12 in a generalised form. The $\mathcal{L}$ matrices are listed in Table 11 for both structures.

Results.

The moments of inertia for V_d symmetry are calculated as 98·32 and 234·34 a.m.u. $\mathring{A}^2$ for I_A and I_B respectively. For V_h symmetry the moment of inertia are I_A 98·32, I_B 185·18 and I_C 283·50 a.m.u. $\mathring{A}^2$. Using the formulae of Badger and Zumwalt for asymmetric tops (mentioned previously) the following band shapes are predicted.

Type A

Type B

Type C.

With symmetric tops the formulae of Gerhard and Dennison (given previously) predict only two types of bands. The parallel band in which the dipole moment is changing parallel to the top axis should appear similar to the corresponding vibration, for V_h symmetry, but the perpendicular bands will have a somewhat smeared out contour.

The selection rules and band shapes for the various vibrations expected for both V_h and V_d symmetry are shown in table 10. The general form of the spectrum is in better agreement with V_d than V_h symmetry as Gayles and Self observed. The 541 cm.$^{-1}$ band clearly belongs either to the B_2 class of V_d or B_{1u} of V_h. The calculations are decisive in placing the 1372 cm.$^{-1}$ band in the E class and the 1155 cm.$^{-1}$ in the B_2.

The intensity ratios (c.f. Table 13) for the active vibrations in both V_h and V_d symmetry were calculated using the previously mentioned method. The localised bond dipole moment derivatives $\frac{(\partial \mu_\beta)}{(\partial R_k)}$ were taken from the literatures values for BF_3,[75] and are included at the base of Table 13.

The infra-red active F$\hat{B}$B deformation (E class for V_d symmetry) is associated with the band observed at 324 cm.$^{-1}$ though its intensity is somewhat low compared with that predicted. The assignment offered by Gayles and Self includes the out of plane B —BF_2 or γ motion which is placed at 657 cm.$^{-1}$, (E class). In the spectra offered in this work the band is overlapped by a doublet of medium intensity which is probably due to an impurity, however, an estimate of the intensity of this band shows it to be approximately one tenth of that predicted. No other band in this region of the spectrum has greater intensity and compared with BF_3 (719 cm.$^{-1}$) the band is certainly low.

It would therefore appear that the band shapes agree best with a V_d structure but the calculations favour V_h. Furthermore if V_d symmetry is assumed the position and intensity of the γ vibration does not agree with predictions. For these reasons consideration was given to the effect of free rotation on the spectrum. Before discussing this however it is worth noting that assistance in solving this problem with the aid of raman spectroscopy was recognised early on. It was not possible to produce sufficient quantities of B_2F_4 however to obtain the liquid or the gas at high pressure. Furthermore multi-path reflection cells were not available and even if they had been it is doubtful whether sufficient improvement could have been obtained. An attempt was made, however, in collaboration with Dr. Beattie of Kings College, London, to obtain the Raman spectrum on a Carey White Spectrometer using one atmosphere of B_2F_4 in a conventional liquid cell adapted for the purpose. With slit widths of 10 cm.$^{-1}$ a broad band was observed at c.a. 680 cm.$^{-1}$, but on continued re-running of the spectrum this band became still broader probably due to decomposition. This is clearly the B-B stretching mode.

Free Rotation.

Longuet-Higgins[76] has shown how the symmetry properties of a molecule may be considered on the basis of nuclear permutations. Though the theory is applicable to rigid molecules, he has shown it to be most useful when free rotation can occur. The symmetry group is defined as the set of all feasible permutations, P, of the positions and spins of identical nuclei and of all PE^* where E^* is the inversion of all particle positions. The complete set of symmetry elements are shown in Figure 17b, The identity operation is denoted by E, a and b refer to the two boron atoms and (12) and (1324) etc. are used to denote cyclic permutations of fluorine atoms 1 and 2, and 1, 3, 2 and 4 respectively. Beneath each element a capital letter is used to denote the particular operation - this is for brevity in constructing the group multiplication table 14. In the Table all operations belonging to the same class are bracketed. The characters χ_i for the group were found by a method described by **Margenau** and Murphy[77]. First, all elements in any class C_i were multiplied by those in C_k and the number of times $h_{ik,j}$ that C_j occurred in the product was noted.

i.e. $C_i C_k = \sum_{j=1}^{s} h_{ik,j}\, C_j$ where s refers to all the classes

If C_i has r_i elements then the χ_i obey the following relationship.

$$r_i\, r_k\, \chi_i\, \chi_k = \chi_1 \sum_{j=1}^{s} h_{ik,j}\, r_j\, \chi_j$$

From this a series of equations are obtained relating the χ_i's with χ_1.

For a group with g elements

$$\sum_{i=1}^{s} \left[\chi_1^{\,i}\right]^2 = g$$

where χ_1^i is the i th irreducible representation in class one. There is usually only one way in which this equation can be satisfied.

With the values of χ_1 the relationships between the χ_i, χ_j and χ_k can be simplified and the numerous sets of linear equations solved for the χ's. The method is long and extremely tedious. The final group obtained for B_2F_4 is shown in Table 15. It is isomorphous with the D_{4h} point group.

Before any comments can be made upon the spectrum it is necessary to determine the number of vibrations and their infra-red activity. The number of vibrations n^{Γ} associated with internal co-ordinate R in species Γ is given by

$$n^{\Gamma} = \frac{1}{g} \sum_{i} g_R \chi_i (R) \chi_i^{\Gamma} (R)$$

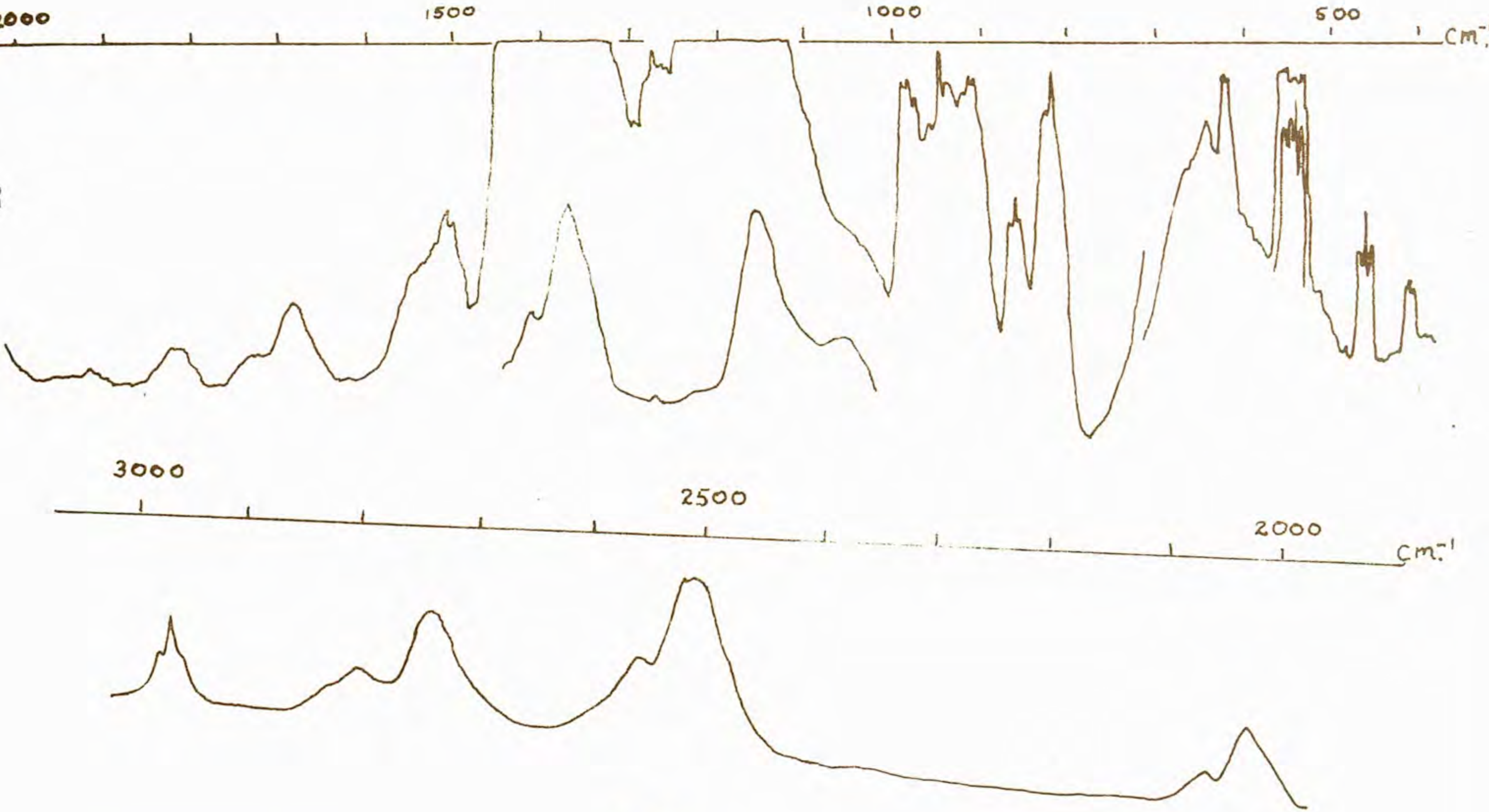
The sum is taken over all the i group operations. g is as defined previously; χ_i is the character in the reducible representation and χ_i^{Γ} its irreducible analogue; g_R is the degeneracy associated with operation i.

Table 16 summarises these calculations together with the redundant symmetry co-ordinates often introduced when a complete set of internal co-ordinates are defined.[78]

It is immediately seen that one pair of B-F stretches and one pair of anti-symmetric in-plane angle bends belong to the degenerate class Γ_9 but the out-of-plane γ mode goes into the other degenerate class Γ_{10}. The full importance of this becomes obvious on considering the classes to which the transition moments μ_x, μ_y and μ_z belong. For it was realised that some permutation elements had equivalent symmetry operations. E^* for example is equivalent to a double reflection in the planes of atoms 1, 2 and 3,4. If allowance is made for the internal rotation about the B-B bond (z axis) the operation (12)(34) is equivalent to a C_2 rotation of the 1, 2 BF_2 units displacements, written $C_2^{1,2}$. $C_2^{\perp}$ is used to represent a rotation about an axis perpendicular to the B-B bond.

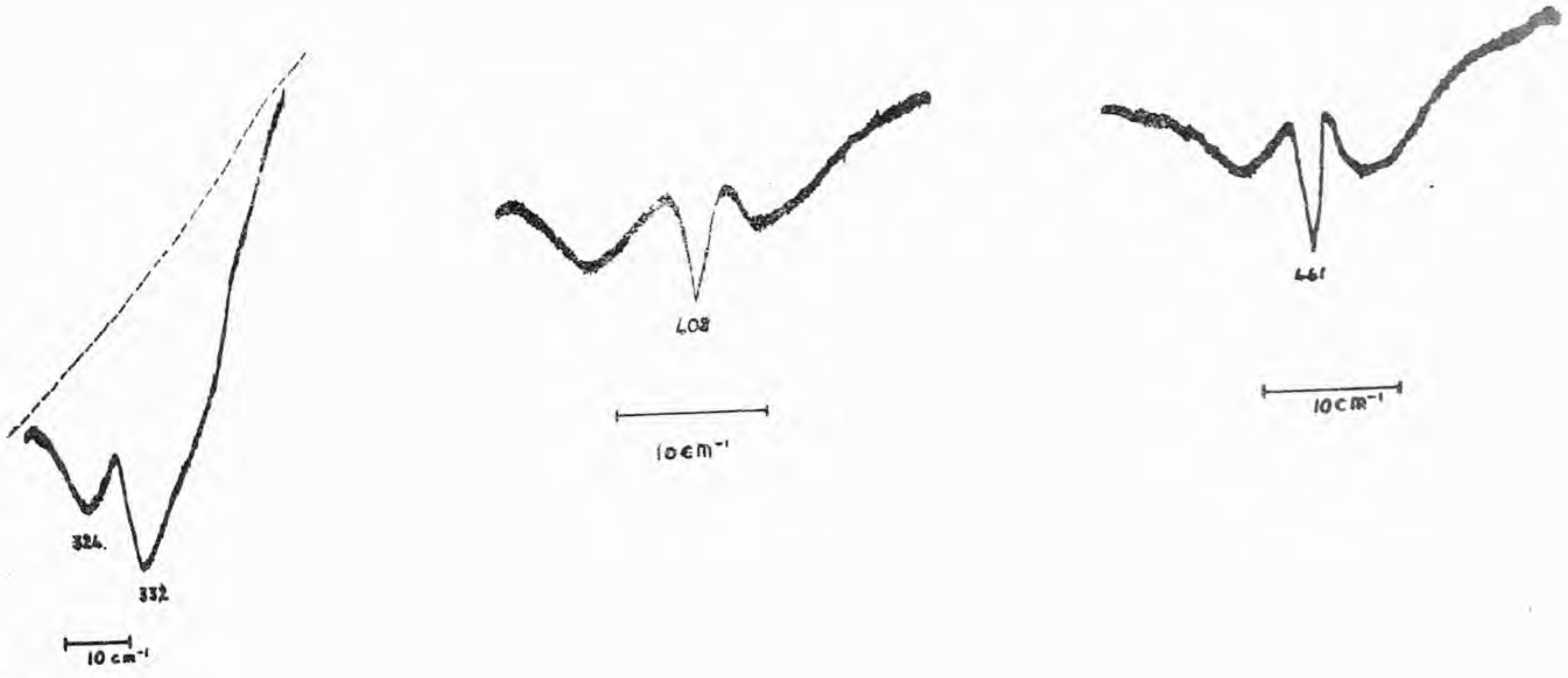
μ_z, therefore, belongs to Γ_3. The transition moments μ_x and μ_y must belong to one of the degenerate species Γ_9 or Γ_{10}, but it is not yet possible to say which. If they belong to Γ_9 then the reason for the reduced intensity of the γ vibration is immediately clear for it will not be an infra-red active vibration. One thing is certain, however, there are fewer infra-red active vibrations for the free rotor.

Since there are no bands between 1000 and 600 cm.$^{-1}$ with the expected intensity, free rotation is certainly possible and even for a shallow potential trough a Boltzmann distribution predicts that most of the molecules will undergo free rotation. Gayles and Self reported the shift of the infra-red active in-plane bend to lower frequencies resulting upon a change to the condensed phase. This is in accord with a free rotor structure for the gas as well as a V_d one. In both cases removal of the degeneracy will lead to a splitting of the frequency components with the lower frequency becoming the ungerade component.



B_2F_4

fig.14.



B_2F_4

fig.15

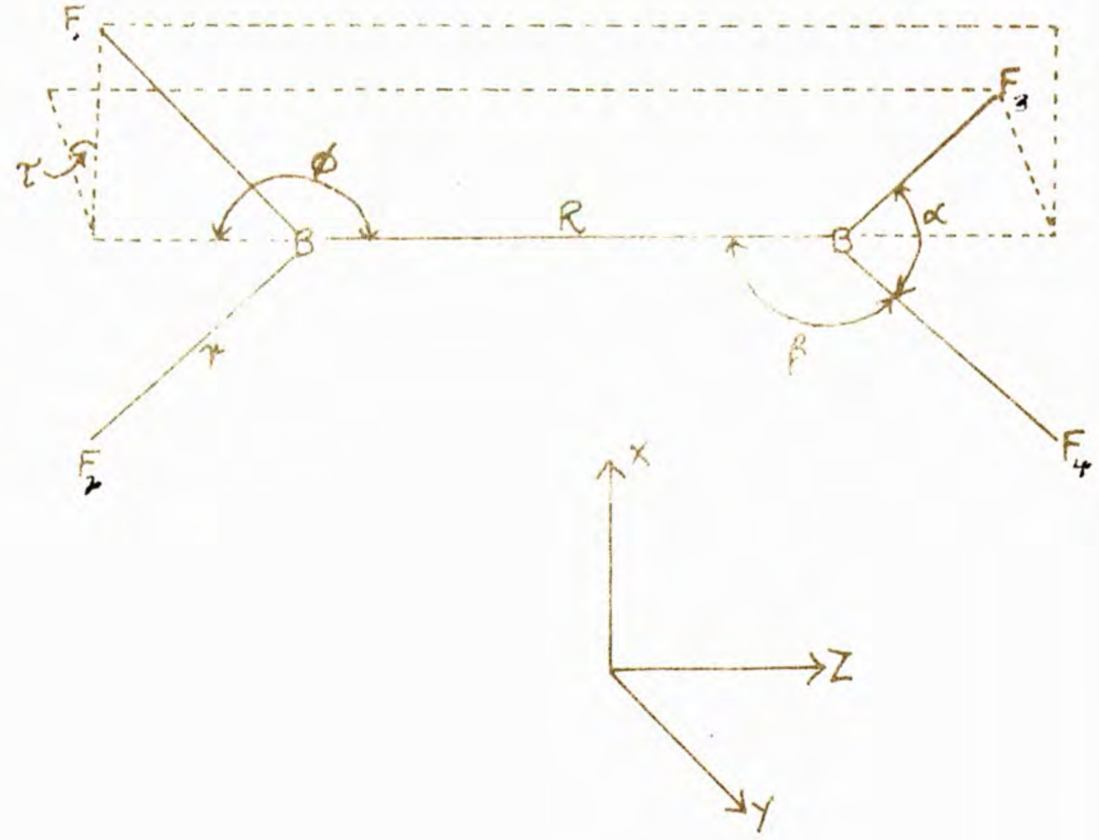


Fig 16

fig 17

B_2F_4 – normal modes. (V_h symmetry)

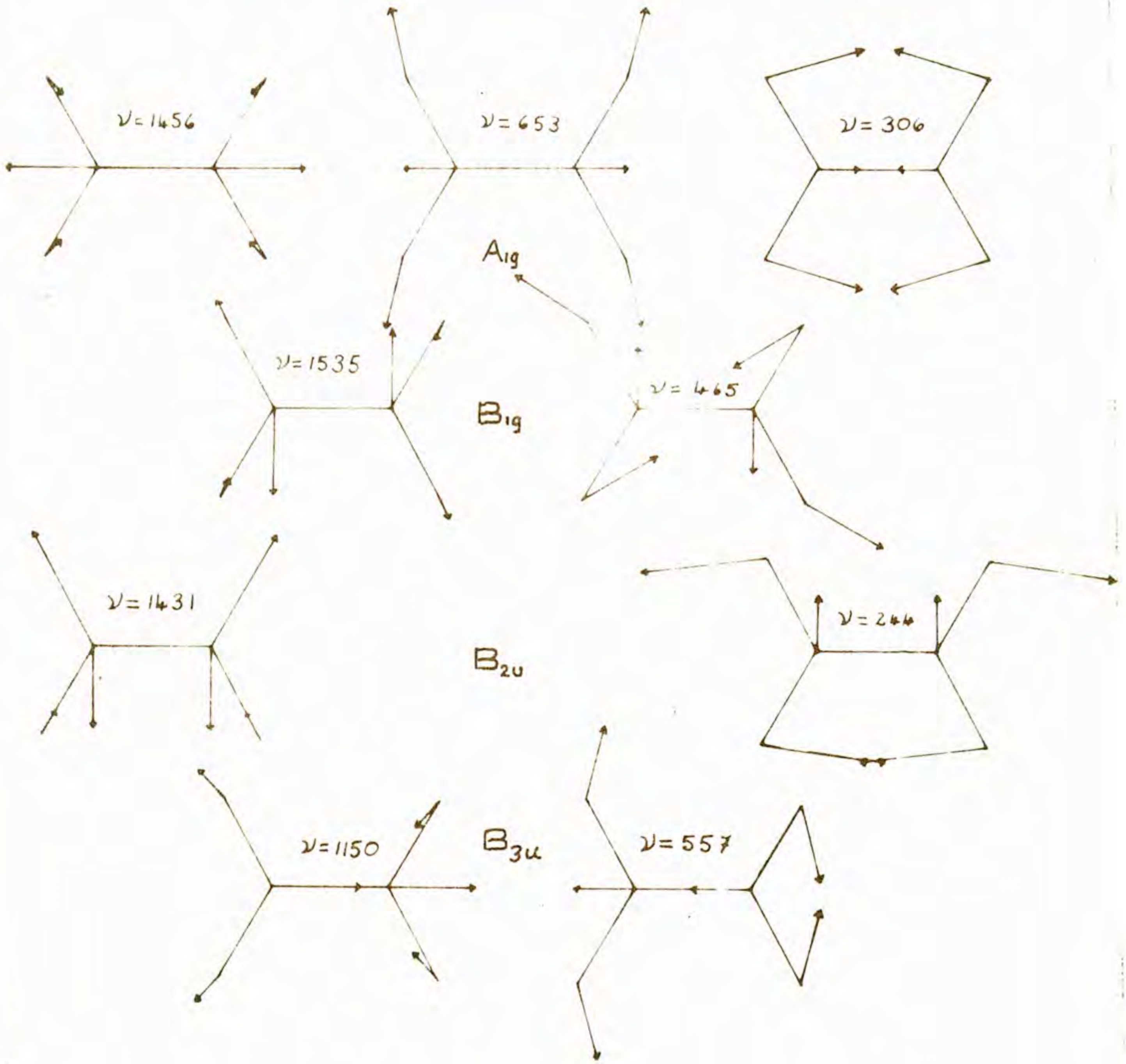
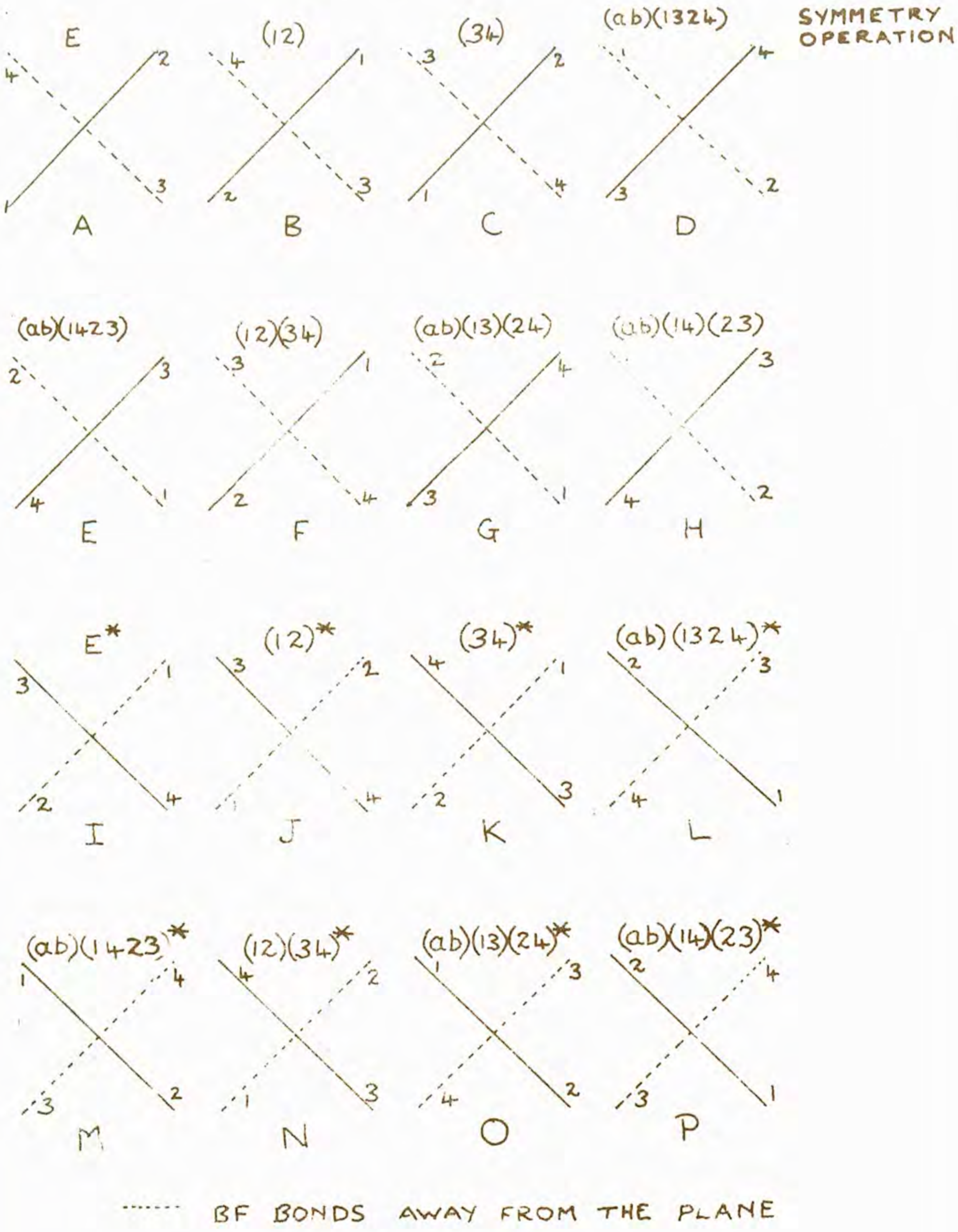


Fig 17b



PERMUTATION OPERATIONS FOR B_2F_4

TABLE 6

FREQUENCY	ASSIGNMENT
2821 vw	2 x 1415
2755 w	2 x 1372
2570 vw	
2515 wm	1372 + 1151
2085 w	
2042 w	
1822 w	1151 + c.a. 660
1732 vw	
1688 w-m	1372 + 324
1548 w	
1415 s	ν_{BF} (^{10}B ^{11}B) E(Γ9) symmetry
1372 vs	ν_{BF} E (Γ9) symmetry
1275 w-m	
1157.5) vs	ν_{BF} B2 (Γ3) symmetry
1151.5)	
986 m Type A	Impurities ?
960 w	
950 w-m Type C	
940	
922 vw	
915 w Type C	
865 w-m Type C	
830 w-m	
821 w-m	

TABLE 6 (Contd.)

c.a.660 w br		B. BF2 deformation ?
642 m		Impurity
621 m		
534	S. Type A	$F\hat{B}B$ deformation B2 (Γ_3) symmetry
541		
543		
548.5		
461 w	Type A	Impurity?
408 w	" A	
331	m	$F\hat{B}B$ deformation E (Γ_9) symmetry
324		

Table 7

Table 8

Force constant		Value BF_3 m-dynes / Å	Value assumed m-dynes / Å
$\mathcal{F}_{1,1}$	$= f_R$	-	3.15
$\mathcal{F}_{1,2}$	$= 2 f_{Rr}$	-	0.0
$\mathcal{F}_{1,3}$	$= 2.3^{-\frac{1}{2}}(f_{R\alpha} - f_{R\beta})$	-	0.0
$\mathcal{F}_{2,2} = \mathcal{F}_{4,4}$	$= f_r + f_{rr}$	8.288	8.288
$\mathcal{F}_{2,3} = \mathcal{F}_{4,5}$	$= 2.3^{-\frac{1}{2}} (f_{r\alpha} - f_{\beta r})$	-	0
$\mathcal{F}_{3,3} = \mathcal{F}_{5,5}$	$= 3^{-1} (2f_\alpha + f_\beta - 4f_{\alpha\beta})$	$f_\alpha - f_{\alpha\alpha} = 0.594$	0.594
$\mathcal{F}_{6,6} = \mathcal{F}_{9,9}$	$= f_r - f_{rr}$	7.220	7.220
$\mathcal{F}_{6,7} = \mathcal{F}_{9,10}$	$= f_{r\beta} - f_{r'\beta}$	$f_{r\alpha} - f_{r'\alpha} = 0.282$	0.282
$\mathcal{F}_{7,7} = \mathcal{F}_{10,10}$	$= f_\beta$	$f_\alpha - f_{\alpha\alpha} = 0.594$	0.594
$\mathcal{F}_{8,8} = \mathcal{F}_{11,11}$	$= f_\phi$	0.866	0.866

Terms involving τ, and interactions involving ϕ assumed negligible.

$$S_1 = \Delta R$$

$$S_2 = \tfrac{1}{2} (\Delta r_1 + \Delta r_2 + \Delta r_3 + \Delta r_4)$$

$$S_3 = \frac{r}{3^{\frac{1}{2}}} (\Delta\alpha_{12} + \Delta\alpha_{34}) - \frac{r}{2.3^{\frac{1}{2}}} (\Delta\beta_1 + \Delta\beta_2 + \Delta\beta_3 + \Delta\beta_4)$$

$$S_4 = \tfrac{1}{2} (\Delta r_1 + \Delta r_2 - \Delta r_3 - \Delta r_4)$$

$$S_5 = \frac{r}{3^{\frac{1}{2}}} (\Delta\alpha_{12} - \Delta\alpha_{34}) - \frac{r}{2.3^{\frac{1}{2}}} (\Delta\beta_1 + \Delta\beta_2 - \Delta\beta_3 - \Delta\beta_4)$$

$$S_6 = \tfrac{1}{2} (\Delta r_1 - \Delta r_2 - \Delta r_3 + \Delta r_4)$$

$$S_7 = \frac{r}{2} (\Delta\beta_1 - \Delta\beta_2 - \Delta\beta_3 + \Delta\beta_4)$$

$$S_8 = \frac{r}{2^{\frac{1}{2}}} (\Delta\phi_{12} - \Delta\phi_{34})$$

$$S_9 = \tfrac{1}{2} (\Delta r_1 - \Delta r_2 + \Delta r_3 - \Delta r_4)$$

$$S_{10} = \frac{r}{2} (\Delta\beta_1 - \Delta\beta_2 + \Delta\beta_3 - \Delta\beta_4)$$

$$S_{11} = \frac{r}{2^{\frac{1}{2}}} (\Delta\phi_{12} - \Delta\phi_{34})$$

TABLE 9

(a) Symmetry V_h

Class	Calc.	Less 5%
Ag	1532	1456
	687	653
	322	306
B_{1u}	1210	1150
	581	557
B_{2u}	1506	1431
	257	244
B_{3u}	830	789
B_{3g}	1615	1535
	490	465
B_{2g}	1366	1298

(b) Symmetry V_d

A_1	1532	1456
	687	653
	322	306
B_2	1210	1150
	581	557
E	1571	1493
	1128	1072
	410	389

TABLE 10

(a) Symmetry $V_h = D_{2h}$

Class	No. of vibs.	Selection rules	i.r. band contours
Ag	3	Raman	-
B_{1g}	0	"	-
B_{2g}	1	"	-
B_{3g}	2	"	-
Au	1 (τ)	Inactive	-
B_{1u}	2	Infra-red	A (PR sep ca 13 cm. $^{-1}$)
B_{2u}	2	"	B (QQ sep ca 10 cm. $^{-1}$)
B_{3u}	1	"	C (PR sep ca 10 cm. $^{-1}$) very pronounced Q branch

(b) Symmetry $V_d = D_{2d}$

Class	No. of vibs.	Selection rules	i.r. band contours
A_1	3	Raman	-
A_2	1 (τ)	Inactive	-
B_1	0	Raman	-
B_2	2	Infra-red and Raman	$\parallel^{el}$(PR sep ca 14 cm. $^{-1}$)
E	3	Raman Infra-red	$\perp$ Q branch intensity 1/5 of that of P and R branches

TABLE 11.

Matrices for the infra-red active fundamentals.

V_h Symmetry.

$$\mathscr{L}(B_{1u}) = 0.6840$$

$$\mathscr{L}(B_{2u}) = \begin{vmatrix} 0.4345, & -0.0013 \\ -0.1802, & 0.2560 \end{vmatrix}$$

$$\mathscr{L}(B_{3u}) = \begin{vmatrix} 0.3038, & 0.0758 \\ -0.5709, & 0.4905 \end{vmatrix}$$

V_d Symmetry.

$$\mathscr{L}(E) = \begin{vmatrix} 0.4146, & 0.1299, & 0.0059 \\ -0.4915, & 0.2919, & 0.3765 \\ -0.3994, & 0.8008, & -0.1227 \end{vmatrix}$$

	x_1	y_1	z_1	x_2	y_2	z_2	x_3	y_3	z_3	x_4	y_4	z_4	x_5	y_5	z_5	x_6	y_6	z_6
Δr_1	$S\bar{\alpha}$	0	$-C\bar{\alpha}$	0	0	0	0	0	0	0	0	0	$-S\bar{\alpha}$	0	$C\bar{\alpha}$	0	0	0
Δr_2	0	0	0	$-S\bar{\alpha}$	0	$-C\bar{\alpha}$	0	0	0	0	0	0	$S\bar{\alpha}$	0	$C\bar{\alpha}$	0	0	0
Δr_3	0	0	0	0	0	0	$CrS\bar{\alpha}$	$SrS\bar{\alpha}$	$C\bar{\alpha}$	0	0	0	0	0	0	$-CrS\bar{\alpha}$	$-SrS\bar{\alpha}$	$-C\bar{\alpha}$
Δr_4	0	0	0	0	0	0	0	0	0	$-CrS\bar{\alpha}$	$-SrS\bar{\alpha}$	$C\bar{\alpha}$	0	0	0	$CrS\bar{\alpha}$	$SrS\bar{\alpha}$	$-C\bar{\alpha}$
ΔR	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-1	0	0	1
$r\Delta\alpha_{12}$	$C\bar{\alpha}$	0	$S\bar{\alpha}$	$-C\bar{\alpha}$	0	$S\bar{\alpha}$	0	0	0	0	0	0	0	0	$-2S\bar{\alpha}$	0	0	0
$r\Delta\alpha_{34}$	0	0	0	0	0	0	$CrC\bar{\alpha}$	$SrC\bar{\alpha}$	$-S\bar{\alpha}$	$-CrC\bar{\alpha}$	$-SrC\bar{\alpha}$	$-S\bar{\alpha}$	0	0	0	0	0	$2S\bar{\alpha}$
$r\Delta\beta_{16}$	$C\beta$	0	$-S\beta$	0	0	0	0	0	0	0	0	0	$\rho-C\beta$	0	$S\beta$	$-\rho$	0	0
$r\Delta\beta_{26}$	0	0	0	$-C\beta$	0	$-S\beta$	0	0	0	0	0	0	$C\beta-\rho$	0	$S\beta$	ρ	0	0
$r\Delta\beta_{35}$	0	0	0	0	0	0	$CrC\beta$	$SrC\beta$	$S\beta$	0	0	0	$-Cr\beta$	$-Sr\rho$	0	$Cr(\rho-C\beta)$	$Sr(\rho-C\beta)$	$-S\beta$
$r\Delta\beta_{45}$	0	0	0	0	0	0	0	0	0	$-CrC\beta$	$-SrC\beta$	$S\beta$	$Cr\rho$	$Sr\rho$	0	$Cr(C\beta-\rho)$	$Sr(C\beta-\rho)$	$-S\beta$
$r\Delta\phi_{12}$	0	$1/2C\alpha$	0	0	$1/2C\alpha$	0	0	0	0	0	0	0	0	$-(\rho+1/C\alpha)$	0	0	ρ	0
$r\Delta\phi_{34}$	0	0	0	0	0	0	$-Sr/2C\alpha$	$Cr/2C\alpha$	0	$-Sr/2C\alpha$	$Cr/2C\alpha$	0	$-Sr\rho$	$Cr\rho$	0	$Sr(1/C\alpha+\rho)$	$-Cr(\rho+1/C\alpha)$	0

C - Cosine   S - Sine $\rho = r/R$ $\bar{\alpha} = \alpha/2$

TABLE.12.

TABLE 13.

Symmetry V_h	V_d	$\nu(V_h)$	$\nu(V_d)$	Intensity V_h	Intensity V_d
B_{1u}	B_2	1150	1150	12.0	12.0
		557	557	2.6	2.6
B_{2u}	E	1431	1493	11.35	9.68
B_{3u}		789	1072	1.55	3.2
		244	389	0.26	0.84

Intensities are given in terms of the $\left(\frac{\partial\mu}{\partial Q}\right)^2$ (D^2/A^{o2}) and not in absolute units.

$$\left(\frac{\partial\mu}{\partial r}\right) = 4.0\ D/\text{Å}$$

$$\left(\frac{\partial\mu}{\partial\alpha}\right) = 2.6\ D.$$

$$\left(\frac{\partial\mu}{\partial\phi}\right) = 1.7\ D.$$

TABLE 14

	I	II		III		IV	V		VI	VII		VIII		IX	X	
	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
A	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
B	B	A	F	G	H	C	D	E	J	I	N	O	P	K	L	M
C	C	F	A	H	G	B	E	D	K	N	I	P	O	J	M	L
D	D	H	G	F	A	E	B	C	L	P	O	N	I	M	J	K
E	E	G	H	A	F	D	C	B	M	O	P	I	N	L	K	J
F	F	C	B	E	D	A	H	G	N	K	J	M	L	I	P	O
G	G	E	D	C	B	H	A	F	O	M	L	K	J	P	I	N
H	H	D	E	B	C	G	F	A	P	L	M	J	K	O	N	I
I	I	J	K	L	M	N	O	P	A	B	C	D	E	F	G	H
J	J	I	N	O	P	K	L	M	B	A	F	G	H	C	D	E
K	K	N	I	P	O	J	M	L	C	F	A	H	G	B	E	D
L	L	P	O	N	I	M	J	K	D	H	G	F	A	E	B	C
M	M	O	P	I	N	L	K	J	E	G	H	A	F	D	C	B
N	N	K	J	M	L	I	P	O	F	C	B	E	D	A	H	G
O	O	M	L	K	J	P	I	N	G	E	D	C	B	H	A	F
P	P	L	M	J	K	O	N	I	H	D	E	B	C	G	F	A

TABLE 15. Free rotor character table

	E	(12) (34)	(ab)(1324) (ab)(1423)	(12)(34)	(ab)(13)(24) (ab)(14)(23)	E*	(12)* (34)*	(ab)(1324)* (ab)(1423)*	(12)(34)*	(ab)(13)(24)* (ab)(14)(23)*
Equiv.	E	C_2^{12}	$C_2^{\perp r}\ C_2^{34}$	$C_2^{12}\ C_2^{34}$	$C_2^{\perp r}$	$\sigma_{12}\sigma_{34}$				
Γ_1	1	1	1	1	1	1	1	1	1	1
Γ_2	1	-1	1	1	-1	1	-1	1	1	-1
Γ_3	1	1	-1	1	-1	1	1	-1	1	-1
Γ_4	1	-1	-1	1	1	1	-1	-1	1	1
Γ_5	1	1	1	1	1	-1	-1	-1	-1	-1
Γ_6	1	-1	1	1	-1	-1	1	-1	-1	1
Γ_7	1	1	-1	1	-1	-1	-1	1	-1	1
Γ_8	1	-1	-1	1	1	-1	1	1	-1	-1
Γ_9	2	0	0	-2	0	2	0	0	-2	0
Γ_{10}	2	0	0	-2	0	-2	0	0	2	0

Reducible Representations for the Internal Co-ordinates.

(Characters are in the same order as those in Table 15).

χ_{BF}	4	2	0	0	0	4	2	0	0	0
χ_{BB}	1	1	1	1	1	1	1	1	1	1
χ_{FBF}	2	2	0	2	0	2	2	0	2	0
χ_{FBB}	4	2	0	0	0	4	2	0	0	0
χ_{γ}	2	0	0	-2	0	-2	0	0	2	0

Distribution of modal types in the various irreducible Representations.

	BF	BB	FBF	FBB		Less Red.	Total No.
Γ_1	1	1	1	1	0	1	3
Γ_2	0	0	0	0	0	0	0
Γ_3	1	0	1	1	0	1	2
$\Gamma_4 - \Gamma_8$	0	0	0	0	0	0	0
Γ_9	1	0	0	1	0	0	2
Γ_{10}	0	0	0	0	1	0	1

TABLE 16

Part 3: The vibrational modes of the Dimethylamino group and the Spectra of $HN(CH_3)_2$ and $B_2[N(CH_3)_2]_4$.

Introduction.

When assigning the spectrum of a complex molecule it is important to take into consideration the degree of coupling between vibrations. In any particular case, say R-Y, certain vibrations of R will be highly sensitive to the effective mass of atom or group Y. It may occur that as the mass alters the frequency of these vibrations may or may not alter considerably. What is most important, however, is that a vibrational frequency that originally applied to an R-Y stretch may now refer to another stretching or even deformation vibration. A satisfactory answer may be had by solving the complete secular equation, though in large molecules this is often not practical. If a more approximate answer is sought the molecules may be considered as a framework to which groups of point mass are attached[31]. This treatment certainly provides useful results but erroneous conclusions are often made when assigning those vibrations that are not isolated to the group or framework. Account of such vibrations may be taken by use of a method, developed by King and Crawford[25] who have shown how $\mathcal{G}$ and $\mathcal{F}$ matrices may be reduced by factoring off modes which are characteristic of a group. The methyl group has been discussed in detail. Two of the C-H deformation modes and the C-H stretching vibrations are factored out leaving only two degenerate deformations modes and the C-X stretching vibration to be considered, X being the atom or group attached to the CH_3.

The following work is concerned with the dimethylamino group attached to an atom or group of varying mass. A comparison for each frequency of the potential energy distribution gives an immediate picture of how the type of vibration and extent of coupling varies with the mass. The extent of the agreement between calculated frequencies of dimethylamine and the observed values will serve as a test both for the validity of the assignment and the usefulness of the model.

Discussion.

Spectroscopic and electron diffraction studies of ammonia, dimethylamine and trimethylamine have indicated a pyramidal structure[31,79,80,81,82]. It would, therefore, seem reasonable to expect this structure to be retained for $(CH_3)_2N$-X derivatives so long as the N retains its trigonal form. The calculations have been based upon C_s symmetry (figure 18), and even though, for steric reasons, the molecule may be slightly displaced from this configuration, the results are expected to suffer little alteration.

The group contains ten atoms and twenty-four fundamentals, of which all are infra-red and raman active. Although the two CH_3 groups produce twelve internal vibrations, the groups are sufficiently separate for only six distinct bands to be anticipated. The others, including the external vibrations of the methyl group, are classed as framework modes following previous methods[25]. Table 17 lists the symmetry co-ordinates for the framework.

The vibrational analysis was carried out by the GF techniques described earlier. The inverse kinetic energy matrix in symmetry co-ordinates $\mathcal{G}$ and the corresponding force constant matrix $\mathcal{F}$, were constructed from the following relationships:-

$$\mathcal{F} = U F U' \quad \ldots\ldots\ldots(1)$$

$$\mathcal{G} = U G U' \quad \ldots\ldots\ldots(2)$$

Where U is defined by equation (3)

(3) ..... $S = U R$ and U' is the transpose of U.

S is the matrix of symmetry co-ordinates and R the corresponding matrix for the internal co-ordinates.

$\mathcal{G}$ and $\mathcal{F}$ are given in tables 18 and 19 respectively. The force constants listed under Table 19 were taken from the literature as were the molecular paramaters beneath Table 18[83]. By allowing X to take on the masses 1, 2, 5, 10, 20 and 100 most of the important substituents are covered. Stretching force constants are rarely outside the range 3-7 mdynes/A° and since the frequency only varies as the square root of the force constant there will be little error in keeping the force constant for the N-X stretch fixed at the value for N-H. Factorisation of the characteristic methyl modes from the complete problem is effected by corrections to $\mathcal{G}$ and $\mathcal{F}$. Following King and Crawford $\mathcal{G}^+$ and $\mathcal{F}^+$ will be used to represent $\mathcal{G}$ and $\mathcal{F}$ in reduced form. The relationship between $\mathcal{F}$ and $\mathcal{F}^+$ is particularly simple

$$(\mathcal{F}^+)_{14,14} = f_{N-X} - 0.06 = (\mathcal{F})_{14,14} - 0.06$$

$$(\mathcal{F}^+)_{17,17} = (\mathcal{F}^+)_{18,18} = (\mathcal{F}^+)_{21,21} = (\mathcal{F}^+)_{22,22} = f_\beta - f_{\beta\beta} + 0.08$$
$$= (\mathcal{F})_{17,17} + 0.08 \text{ etc.}$$

In $\mathcal{G}^+$ the corrections take the form of changes to the effective masses of the moving atoms. These changes are non isotropic. Excluding the methyl rocking co-ordinate the correction changes to effective reciprocal carbon mass along the C_{3v} axis (μ_c^z) of the methyl group to 0.0676 a.m.u.$^{-1}$ and along the perpendicular axes ($\mu_c^{x,y}$) to 0.0727 a.m.u.$^{-1}$ For the methyl rocking modes μ_c takes on the $\mu_c^{x,y}$ value above and

$\mu_H^+ = 0.7361 + 0.790a - 0.014a^2$ where a is the ratio of the CH bond length to the C-N bond length. Off diagonal $\mathcal{G}^+$ elements are computed from equations 20 and 33 in reference 25.

The solution of the secular equation:-

$$\mathcal{G}^+\mathcal{F}^+\mathcal{L}^+ - \mathcal{L}^+\Lambda^+ = 0$$

was achieved by computer methods.

The eigenvector matrix $\mathcal{L}^+$ is related to the normal co-ordinate matrix Q^+ and matrix S previously defined by

$$S = \mathcal{L}^+ Q^+ \text{ ....(4)}$$

eigenvalues $\lambda_1 \text{ ....} \lambda_n$

Λ^+ is the diagonal matrix of the non-characteristic eigenvalues for the methyl group.

In order to interpret a particular mode in terms of the familiar bond stretch or deformation vibration it was decided to follow the method of Morino and Kachitsu[84] by determining how the potential energy is distributed among the symmetry co-ordinates. That the distribution for a particular normal co-ordinate is represented by $\mathcal{L}'\mathcal{F}\mathcal{L}$ is easily seen.

$2V = R'FR = S'UFU'S$ by 3

using equations 1 and 4 $2V = Q'\mathcal{L}'\mathcal{F}\mathcal{L}\,Q$.

Table 20 lists the values for $\mathcal{L}'\mathcal{F}\mathcal{L}$ in percentage form. Since $\mathcal{F}^+$ is essentially diagonal only the terms $(\mathcal{F}^+)_{i,i}\,(\mathcal{L}^+)^2_{i,n}$ have been evaluated.

Results.

It is immediately obvious from Table 20 that some frequencies will remain constant for any substitution. Two of the three methyl rocking modes in particular remain very pure and quite constant in frequency. In fact the A'' rocking modes alter less tha 1 cm.$^{-1}$ for an increase M_x from 5 to 100 a.m.u. The anti-symmetric CN stretch also shows this marked indepencence of M_x. The small shifts which do occur are all in the sense expected for small kinetic interactions with the deformation mode and are in complete agreement with the interpolation rules. The lower frequency A' rock mode is extremely mass sensitive and for $M_x > 5$ the mode is strongly mixed with CN and NX stretching modes. The higher frequency rock vibration is very constant in frequency dropping monotonically from 1226 cm.$^{-1}$ for $M_x = 1$ to 1210 cm.$^{-1}$ for $M_x = 100$. Variations in frequency and percentage potential energy arising from rocking modes (β modes) are graphed against mass in Figures 19a and b. Rather surprisingly the principal mixing of the N-X stretch occurs with one of the β modes. For large masses the two vibrations become indistinguishable.

Dimethylamine.

Comparison of these results for dimethylamine with a previous assignment[83] show that little alteration is required (c.f. Table 21). The A' band calculated at 1226 cm.$^{-1}$ is observed at 1245 cm.$^{-1}$ and is mainly a methyl deformation. The N-H stretch calculated at 3349 cm.$^{-1}$ is observed at 3355 cm.$^{-1}$. The bands assigned to the A' and A'' CN stretch and A' C_2N deformation at 930 and 1024, and 397 cm.$^{-1}$ agree well with the calculations. The band centred at 1155 cm.$^{-1}$ appears to be complex. From the calculations it appears that two vibrations must be assigned to this band; the A' and A'' CH_3 deformations that are calculated at 1159 and 1157 cm.$^{-1}$ respectively. In order to verify this, the low temperature work of Stewart[85] was repeated using a similar cell[86], but to be certain that the sample of dimethylamine was in a crystalline form it was annealed by permitting the temperature to rise to about twenty or thirty degrees below the melting point and then slowly cooled to -196°. The process was repeated until the spectrum remained unchanged. The spectrum obtained agreed with that reported previously. The salient features of this work are that (i) the band observed at 1155 cm.$^{-1}$ in the gas splits into two in the solid, one at 1150 and the other at 1175 cm.$^{-1}$ The failure to observe splitting in other bands indicates that these components must result from the two vibrations previously mentioned and are not crystal splittings; (ii) the band at 724 cm.$^{-1}$ in the gas moves to 882 cm.$^{-1}$ in the solid. Such a large shift would be expected if, as appears quite reasonable, this band is an N-H deformation pushed to higher frequencies in the solid by hydrogen bonding. Previously[83] this band was assigned to the anti-symmetric N-H deformation, however the calculations lead to an unequevocable assignment in the A' class. The A'' N-H deformation made is calculated at 1390 cm.$^{-1}$ and is probably one of the bands in the 1400 cm.$^{-1}$ region. It might well be the band observed at 1430 cm.$^{-1}$ in the solid though it is difficult to understand why a shift equivalent to that for the A'' band is not observed and this peak could therefore equally well belong to one of the methyl deformation modes.

The only band not characteristic of the CH_3 group which now remains to be assigned is the one calculated at 1048 cm.$^{-1}$. No band was observed in this region by Barcelo and Bellanato[83] but other workers have seen a weak absorption near here[87] and a band of medium intensity is observed in the raman[88] at 1078 cm.$^{-1}$. This band is a methyl deformation vibration of the A'' class. The selection rules lead one to expect this vibration to be both raman and infra-red active. It is difficult to see why this band does not appear more strongly in the infra-red.

Apart from the low frequency CH_3 twisting mode the remaining vibrations are characteristic of the methyl group. For standard CH_3X molecules they have been calculated at 2932 and 3051 cm.$^{-1}$ for the symmetric and degenerate stretching vibrations respectively,[25] and at 1378 and 1451 for the methyl deformations which belong to the symmetric and degenerate classes respectively. The deformation vibrations were observed as strong bands with peaks at 1404, 1466 and 1496 cm.$^{-1}$. The low frequency band is probably the symmetric vibration and the two at higher frequencies are the components of the degenerate vibration split by the lower symmetry of dimethylamine. In the region of the C-H stretch it is difficult to be certain. The bands at 1400 are extremely intense and their overtones and combination bands may mix in considerably with the C-H stretching modes. If no mixing occurs between the stretching modes of the two methyl groups only two bands should be oserved, the 2932 and 3051 cm.$^{-1}$. If the degeneracy of the 3051 peak is lifted by symmetry considerations then there will be one more peak. Five are observed. It would therefore appear possible that there is some coupling between methyl groups or alternatively that Fermi resonance is occurring with overtones and combination bands involving the methyl deformation bands. For example the 2967 cm.$^{-1}$ could be a combination of the 1496 and 1466 also the 2802 cm.$^{-1}$ could be the first overtone of that at 1404 cm.$^{-1}$.

Finally the discrepancy between the observed and calculated frequencies for the C-N stretch modes may be used to evaluate the interaction force constant $f_{CN/CN}$ by a perturbation treatment.

It may be shown[59] that $\mathcal{L}'\mathcal{F}\mathcal{L}=\Lambda$ and if a small perturbation in $\mathcal{F}$ is permitted then

$$\mathcal{L}'(\mathcal{F}+\Delta\mathcal{F})\mathcal{L}=\Lambda+\Delta\Lambda$$

if the valid assumption is made that small variations in $\mathcal{F}$ have little effect on $\mathcal{L}$ and $\mathcal{L}'$. Using the original relationship $\mathcal{L}'\mathcal{F}\mathcal{L}=\Lambda$ then gives the desired relationship

$$\mathcal{L}'\Delta\mathcal{F}\mathcal{L}=\Delta\Lambda$$

f_{CN} was found to be -0.02 mdynes/A°, and $f_{CN/CN}$ to be -0.004 mdynes/A°. Hence f_{CN} = 4.598 mdynes/A° and $f_{CN/CN}$ = 0.636 mdynes/A°.

Since neither of the CN stretching vibrations contribute more than 70% towards the respective A' and A'' modes it is realised that a better approximation would be had by allowing other force constants to vary, but this would entail using extra data which was not available.

Tetrakis (dimethylamino) diboron $B_2[N(CH_3)_2]_4$

This compound has been studied by Becher et al[24] in the infra-red and raman. On steric grounds the overall symmetry is not expected to be above D_2, and comparison of the infra-red and raman indicates that the effective symmetry is not lower.

Varying degrees of approximation can be employed in interpreting the spectra of this molecule. Becher discusses the B_2N_4 skeleton vibrations in some detail. This still leaves undecided the degree of coupling between the dimethylamino group and the skeleton. To determine the extent of this we may consider the spectra in the light of the previous calculations. The effective mass of the skeleton attached to the $-N(CH_3)_2$ group must be greater than 11 a.m.u. but it is unlikely to exceed 20 a.m.u. This would lead us to anticipate the fundamentals in the range

CH_3 rocking modes	A' 1220-1200 $cm.^{-1}$
" " "	A'' c.a. 1160 and c.a. 1050 $cm.^{-1}$
CH_3 umbrella mode	A' and A'' 1378 $cm.^{-1}$
CH_3 antisymmetric deformation	A' and A'' 1450 $cm.^{-1}$
CNC deformation	A' 430-400 $cm.^{-1}$
CNB deformation	A' 350-310 $cm.^{-1}$
" "	A'' 600-540 $cm.^{-1}$
CH_3 rocking mode	A' 1500-1400 $cm.^{-1}$
CN stretch	A' 990-970 $cm.^{-1}$
NX stretch	A' 900-790 $cm.^{-1}$
CN stretch	A'' c.a. 1000 $cm.^{-1}$

That the B-N stretch and CH_3 rock are quite sensitive to mixing may be seen from Table 20. This could well result in mixing between the CH_3 rocking modes of different dimethylamino groups. Table 22 lists the frequencies reported in reference 14.

Two intense polarised raman lines occur at 586 and 1376 $cm.^{-1}$. The former must certainly arise from the B-B stretching vibration, but these are two contenders for the latter. These are the internal deformation of the CH_3 group that is predicted at 1378 $cm.^{-1}$, and the symmetric BN stretch as suggested in reference 14. It is most probable that the band is due to the latter mode but with some contribution from the methyl vibration. In the infra-red the band is found at 1367 $cm.^{-1}$. The two bands calculated near 420 and 330 $cm.^{-1}$ are good examples of the coupling which may arise. Both contain 50% CNB and NC_2 deformation vibrations of the A' class of X-NMe$_2$ for $M_x = 10$. If the dimethylamino groups in the diboron compound are vibrating almost independently of one another, which is reasonable, these vibrations will behave like a symmetric group vibration and appear as polarised lines in the raman. Two polarised raman lines are observed at 385 and 352 cm.$^{-1}$. If during this vibration the boron has an effective mass greater than 11 the 385 cm.$^{-1}$ line will belong to the NC$_2$ and the 362 cm.$^{-1}$ to the CNB deformation. Previously both were assigned to NC$_2$ deformations. Five or four more vibrations below 600 cm.$^{-1}$ are now expected: two BN$_2$, one or two NB$_2$ and one CNB deformation vibrations. The BN$_2$ mode will be degenerate for V_d symmetry, and the assumption of negligible coupling between dimethylamino groups is again assumed. The symmetric BN$_2$ deformation mode appears at 254 cm.$^{-1}$ in the raman and 259 cm.$^{-1}$ in the infra-red. The antisymmetric CNB deformation could be the 608 or 567 cm.$^{-1}$ bands. Previous calculations however fix the 608 cm.$^{-1}$ band as an antisymmetric BN$_2$ deformation. Although for most of the vibrations, the dimethylamino groups will be independent, it is likely that there will be some coupling through the common boron atoms for the NC$_2$ deformation and NC stretching modes. The extra vibration for the deformation mode is assigned to the infra-red band at 460 cm.$^{-1}$. The extra CN stretching modes produced by the coupling will probably be weak and are assigned provisionally to the bands at 892 cm.$^{-1}$ for the symmetric and 1128 cm.$^{-1}$ for the antisymmetric. The degenerate NB$_2$ deformation (V_d symmetry) will split for V or V_h symmetry and is assigned to the bands at 285 and 318 cm.$^{-1}$

With the aid of Table 20 the band observed as a polarised raman line of moderate intensity at 973 cm.$^{-1}$ is assigned to the CN stretching vibration. Similarly, the band at 1216 cm.$^{-1}$ is assigned to the A' and the 1186 and 1066 cm.$^{-1}$ to the A'' methyl deformation modes. The band observed at 1409 cm.$^{-1}$ in the infra-red which appears as an intense line in the raman must be the antisymmetric B-N stretch.

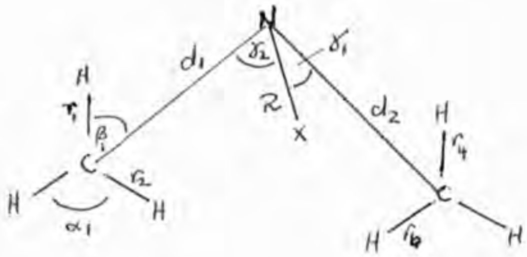
Two further bands due to the $-N(CH_3)_2$ moiety are expected near 1000 cm.$^{-1}$, the antisymmetric CN stretch computed to be near 1000 cm.$^{-1}$ and the mixed BN stretch/CH_3 rock mode computed as 900 to 800 cm.$^{-1}$. Both bands might be expected to have reasonable infra-red intensity, and the former in particular would be expected to have a similar frequency in $B[N(CH_3)_2]_3$. The lack of infra-red bands in the range 1050 - 900 cm.$^{-1}$ is surprising. It must be assumed that the 892 cm.$^{-1}$ band is due to the antisymmetric CN stretch. A frequency higher than 1100 cm.$^{-1}$ is unacceptable in view of the fact the mode is identified with a frequency of 1024 cm.$^{-1}$ in $(CH_3)_2NH$. An investigation of the infra-red spectra of tetrakis (dimethylamino) diboron was carried out and confirmed all details of spectra recorded by Becher. The lack of another candidate for the mixed CN/BN/β mode near 900 cm.$^{-1}$ necessitates the assignment of the 832 cm.$^{-1}$ band as this A' fundamental mode (the infra-red band was observed in this work to be a doublet with frequencies 830 and 839 cm.$^{-1}$).

There remains only one antisymmetric B-N stretching vibrationaand two out of plane boron modes. The former is most likely the intense band observed at 1117 cm.$^{-1}$ in the infra-red. It appears as a weak band in the raman and is also to be found in the spectrum of $B[N(CH_3)_2]_3$. The out of plane vibrations are probably the 639 or 608 $cm.^{-1}$ bands and the second component of the 830 $cm.^{-1}$ doublet.

The band at 1343 $cm.^{-1}$ is possibly a coupled vibration involving B-N stretching modes.

The C-H stretching modes must be associated with the four bands at 2798, 2862, 2870 and 2890 $cm.^{-1}$ which appear quite intense in both raman and infra-red. Other high frequency bands are perhaps overtones and combination bands or if the methyl group is not vibrating completely independently, i.e. as a CH_3Y molecule the degenerate stretching modes will split the two components. Any other strong bands in this region could perhaps be traced to Fermi resonance, involving the C-H stretching modes and overtones or combination bands of the strong absorptions below 1500 $cm.^{-1}$.

In conclusion it may be said that the assistance to be had from calculations of the type depicted are invaluable. The gross measure of agreement for dimethylamine certainly justifies the continued use of the model for more complicated molecules.



$R = 1.01$ Å

$r = 1.08$ Å

$d = 1.46$ Å

$\alpha = \beta = \gamma = 109^\circ\ 28'$

fig 18

Internal Co-ordinates.

R_1 —— R_6) involve iso-
R_{10} —— R_{15}) lated CH_3 vibrations

$R_7 = \Delta d_1$

$R_8 = \Delta d_2$

$R_9 = \Delta R$

$R_{16} = r \Delta \beta_1$

$R_{17} = r \Delta \beta_2$

R_{18} = ..."...

R_{19} = ..."...

R_{20} = ..."...

$R_{21} = r \Delta \beta_6$

$R_{22} = d \Delta \gamma_1$

$R_{23} = d \Delta \gamma_2$

$R_{24}\quad d \Delta \gamma_3$

Fig 19 a.

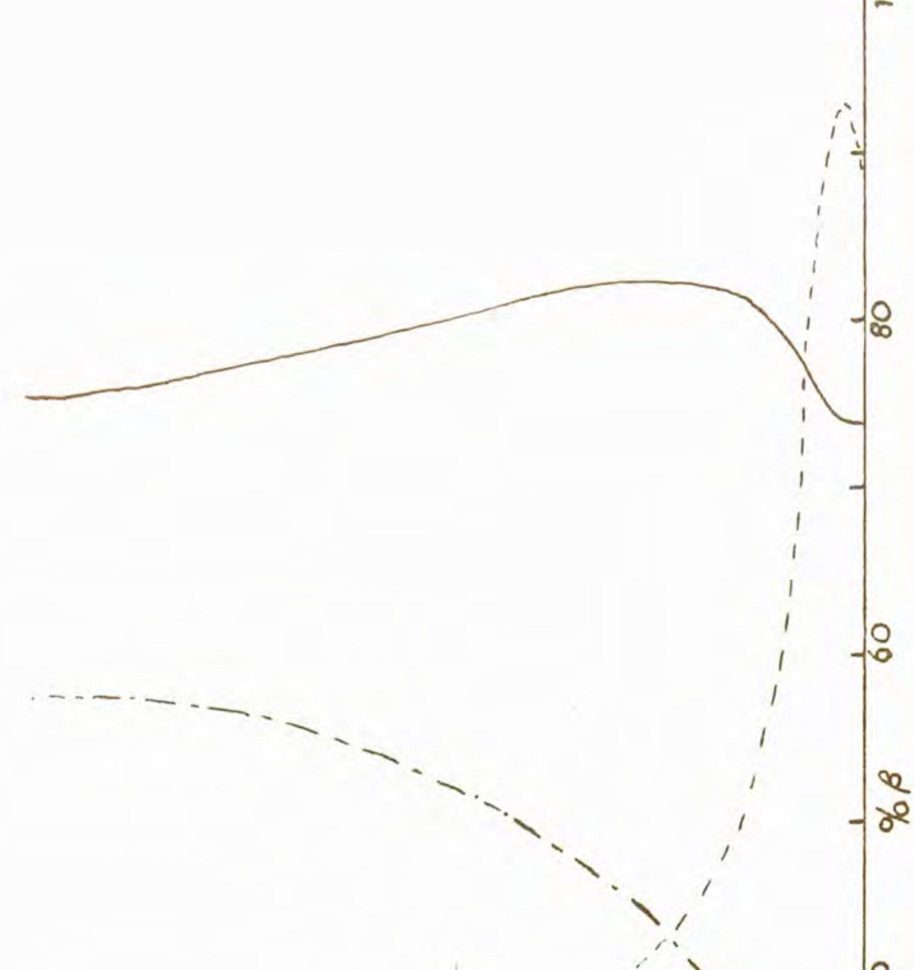
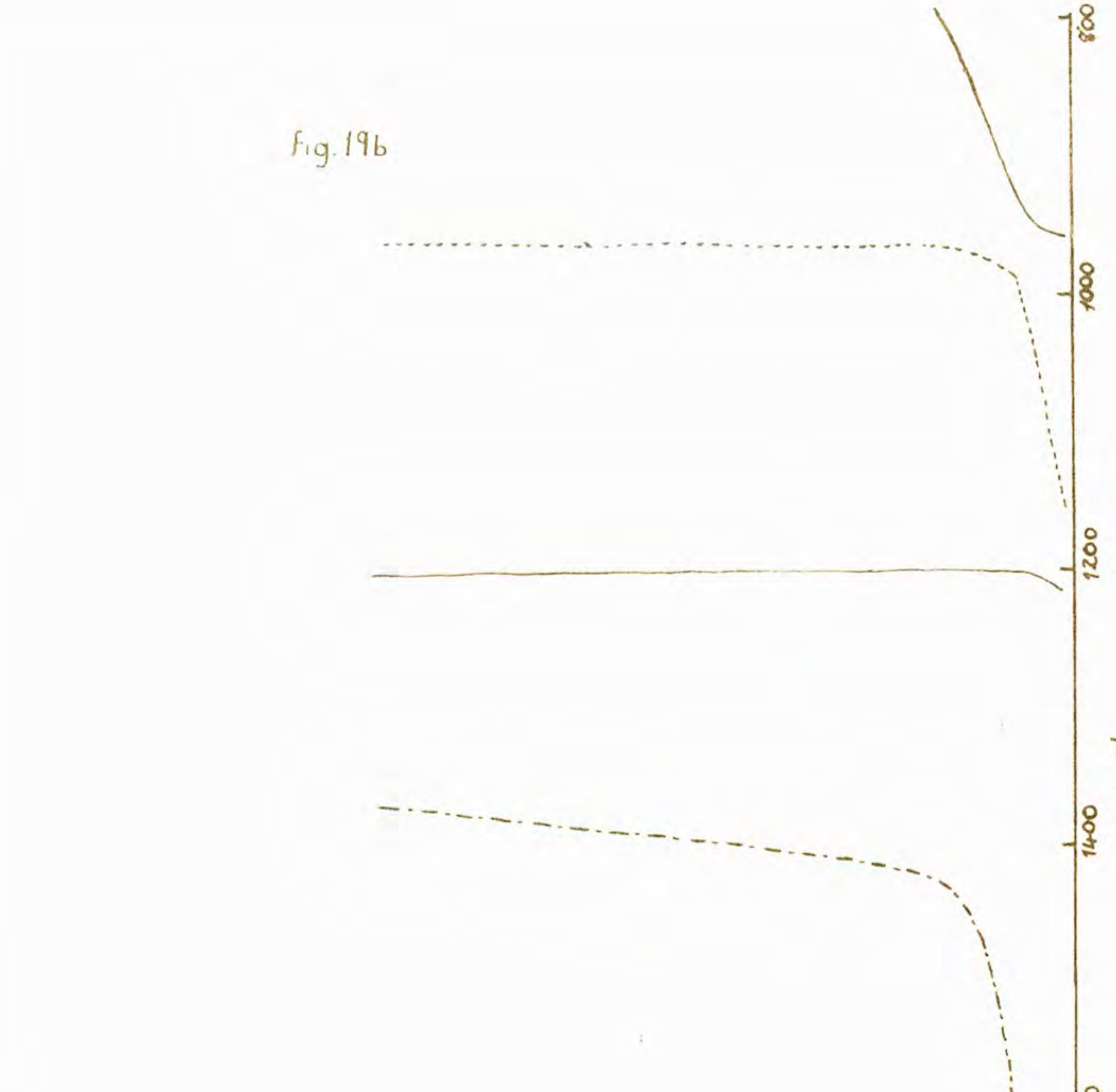


Fig. 19b



$$
\begin{array}{c|cccccccccccc}
 & R_7 & R_8 & R_9 & R_{16} & R_{17} & R_{18} & R_{19} & R_{20} & R_{21} & R_{22} & R_{23} & R_{24} \\
S_{13} & 1/2^{\frac{1}{2}} & 1/2^{\frac{1}{2}} & & & & & & & & & & \\
S_{14} & & & 1 & & & & & & & & & \\
S_{15} & & & & & & & & & & 1/2^{\frac{1}{2}} & & \\
S_{16} & & & & & & & & & & & & 1 \\
S_{17} & & & & 1/3^{\frac{1}{2}} & 1/2\cdot3^{\frac{1}{2}} & 1/2\cdot3^{\frac{1}{2}} & 1/3^{\frac{1}{2}} & 1/2\cdot3^{\frac{1}{2}} & 1/2\cdot3^{\frac{1}{2}} & & & \\
S_{18} & & & & & \frac{1}{2} & -\frac{1}{2} & & -\frac{1}{2} & \frac{1}{2} & & & \\
\hline
S_{19} & 1/2^{\frac{1}{2}} & 1/2^{\frac{1}{2}} & & & & & & & & & & \\
S_{20} & & & & & & & & & & 1/2^{\frac{1}{2}} & -1/2^{\frac{1}{2}} & \\
S_{21} & & & & 1/3^{\frac{1}{2}} & 1/2\cdot3^{\frac{1}{2}} & 1/2\cdot3^{\frac{1}{2}} & -1/3^{\frac{1}{2}} & 1/2\cdot3^{\frac{1}{2}} & 1/2\cdot3^{\frac{1}{2}} & & & \\
S_{22} & & & & & \frac{1}{2} & -\frac{1}{2} & & \frac{1}{2} & -\frac{1}{2} & & &
\end{array}
$$

U MATRIX FOR FRAMEWORK OF $(CH_3)_2N\text{-}X$

TABLE 17

$\mu_C + \frac{2}{3}\mu_H$	$-\frac{2^{1/2}}{3}\mu_H$	$\frac{2^{1/2}}{3}\mu_H(1-d/R)$	$-\frac{4}{3}\mu_H$	$\frac{1}{3^{1/2}}\mu_H r/d$	$\mu_H r/d$
	$\mu_H + \mu_X$	$-\frac{4}{3}\mu_H$	$\frac{2^{3/2}}{3}\mu_H$	$-\frac{4\cdot 2^{1/2}}{3^{1/2}}\mu_H r/d$	0
		$\mu_C + \mu_X/2\, d^2/R^2$ $+\mu_H(11/6 + d/3R + d^2/2R^2)$	$-\frac{1}{3\cdot 2^{1/2}}\left\{4\mu_H(1-d/R) + 3\mu_C\right\}$	$\frac{1}{6^{1/2}}\left\{2\mu_H(r/d + r/R) + \mu_C/2(1+3r/d)\right\}$	$-\frac{1}{2^{1/2}}\left\{2\mu_H(7r/6R + 5r/6d) + \mu_C/2(1+3r/d)\right\}$
			$2\mu_C + 8/3\,\mu_H$	$-\frac{1}{2\cdot 3^{1/2}}\left\{4\mu_H r/d + \mu_C(3r/d + 1)\right\}$	$-\frac{1}{2}\left\{4\mu_H r/d + \mu_C(3r/d+1)\right\}$
				$\mu_H + 11/4\,\mu_H r^2/d^2$ $+\mu_C(1/6 + r/d + 3r^2/2d^2)$	$-\frac{3^{1/2}}{4}\mu_H r/d$
					$\mu_H + 9/4\,\mu_H r^2/d^2$ $+\mu_C(1/6 + r/d + 3r^2/2d^2)$

A′

$\mu_C + 4/3\,\mu_H$	$2^{1/2}\mu_H(1/3 + d/R)$	$-\frac{1}{3^{1/2}}\mu_H r/d$	$-\mu_H r/d$
	$\mu_C + 3/2\,\mu_X d^2/R^2$ $+\mu_H(1/6 + d/R + 3d^2/2R^2)$	$\frac{1}{6^{1/2}}\left\{\mu_H(r/R - r/d) - \mu_C/2(1+3r/d)\right\}$	$\frac{1}{2^{1/2}}\left\{\mu_H(r/d - r/R) + \mu_C/2(1+3r/d)\right\}$
		$\mu_H + \mu_H r^2/4d^2$ $+\mu_C/2(1/6 + r/d + 3r^2/2d^2)$	$\frac{3^{1/2}}{4}\mu_H r^2/d^2$
			$\mu_H + 3/4\,\mu_H r^2/d^2$ $+\mu_C(1/6 + r/d + 3r^2/2d^2)$

A″

$d = 1{\cdot}46$ Å ; $r = 1{\cdot}08$ Å ; $R = 1{\cdot}01$ Å

$\mathcal{G}$ for $XN(CH_3)_2$

TABLE - 18

A'

$f_d + f_{dd}$	$2^{\frac{1}{2}}f_{d,R}$	$f_{d\gamma} +$ $f_{d'\gamma}$	$2^{\frac{1}{2}}f_{d'\gamma}$	0	0
	f_R	$2^{\frac{1}{2}}f_{R\gamma}$	$f_{R\gamma'}$	0	0
		$f_\gamma +$ $f_{\gamma\gamma}$	$2^{\frac{1}{2}}f_{\gamma\gamma'_1}$	0	0
			$f_{\gamma'}$	0	0
				$f_\beta - f_{\beta\beta}$	0
					$f_\beta - f_{\beta\beta}$

A''

$f_d - f_{d,d}$	$f_{d'\gamma} - f_{d\gamma}$	0	0
	$f_\gamma - f_{\gamma\gamma}$	0	0
		$f_\beta - f_{\beta\beta}$	0
			$f_\beta - f_{\beta\beta}$.

f_β = 0.61 mdynes/Å

f_d = 4.6 " "

f_R = 6.2 "

$f_{d,d}$ = 0.64 "

$f_{d,R}$ = 0.1 "

$f_{\gamma'_1}$ = 0.45 "

f_γ = 0.31 "

other force constants taken to be zero.

TABLE 19

TABLE 20: DISTRIBUTION OF POTENTIAL ENERGY

MASS: 1 A.M.U.

VIBRATION	FREQ.	3349	1227	1159	967	796.5	388	1390	1157	1048	982 cm.$^{-1}$
CN		1	17	3	68	0	5	0	33	9	60
NX		99	0	0	0	0	0				
CNX		0	5	4	3	88	1	100	6	0	0
CNC		0	4	1	2	1	92				
HCN		0	1	88	9	2	1	0	1	68	25
HCN		0	73	3	18	8	2	0	60	23	15

MASS: 2 A.M.U.

		2462	1220	1133	965	618	384	1162	1060	1010	981 cm.$^{-1}$
CN		0	17	2	70	2	5	30	9	5	57
NX		98	1	2	0	0	0				
CNX		0	3	2	1	90	2	2	22	74	3
CNC		0	5	1	2	3	90				
HCN		2	0	91	7	2	0	5	67	7	28
HCN		0	74	2	21	3	3	63	1	15	12

MASS: 5 A.M.U.

		1768	1215	1057	958	477	369.5	1160	1051	983	736 cm.$^{-1}$
CN		2	14	0	74	5	4	31	9	60	0
NX		85	3	13	1	6	0				
CNX		1	3	0	0	71	17	0	0	0	100
CNC		1	5	0	2	16	75				
HCN		11	0	87	1	1	0	6	70	25	0
HCN		0	75	0	22	1	4	63	21	15	0

MASS: 10 A.M.U.

VIBRATION FREQ.	1528	1213	987	907	429	349	1160	1051	983	614 cm.$^{-1}$
CN	5	12	29	40	1	3	31	9	60	0
NX	64	0	9	27	2	0				
CNX	1	3	0	0	50	46	0	0	0	100
CNC	2	4	0	1	46	47				
HCN	27	2	51	23	0	0	6	70	25	0
HCN	0	78	12	8	0	5	63	21	15	0

MASS:20 A.M.U.

	1432	1211	975	791	402	310	1160	1051	983	543 cm.$^{-1}$
CN	8	11	51	17	2	1	31	9	60	0
NX	46	0	3	48	3	1				
CNX	1	3	0	2	17	77	0	0	0	100
CNC	3	4	1	0	77	16				
HCN	41	4	27	31	0	0	6	70	25	0
HCN	0	78	18	2	0	4	63	21	15	0

MASS: 100 A.M.U.

	1376	1210	972	643	379	234	1160	1050	983	478 cm.$^{-1}$
CN	4	13	65	13	2	1	31	9	60	0
NX	31	6	1	49	5	11				
CNX	1	3	0	12	0	82	0	0	0	100
CNC	3	3	1	1	90	3				
HCN	49	5	17	24	0	0	6	70	25	0
HCN	1	70	16	1	2	3	63	21	15	0

TABLE 21

DIMETHYLAMINE.

FUNDAMENTAL FREQUENCIES

	OBSERVED IN GAS	ASSIGNMENT
	3355 $cm.^{-1}$	A' NH stretch
	2967	A''(1496 + 1466) or CH stretch
	2912	A'' CH stretch
	2855	A' CH stretch
	2802	A'(2 x 1404) or CH stretch
	1496	A'' CH_3 deformation
	1466	A' CH_3 deformation
	1404	A' CH_3 deformation
	1245	A' CH_3 deformation
Splits into 1150 and 1178 $cm.^{-1}$ in solid	1155	A' and A'' CH_3 deformation
weak in infra-red medium raman	1078	A'' CH_3 deformation
	1024	A'' CN stretch
	930	A' CH stretch
moves to 882 in in solid	724	A' N-H deformation
	397	A' C_2N deformation
	290	CH_3 twisting
	250	CH_3 twisting

TABLE 22

TETRAKIS (DIMETHYLAMINO) DIBORON

FUNDAMENTAL FREQUENCIES.

Raman	Infra-red	Assignment
254 m	259 m	BN_2 deformation
	285 v.w.	NB_2 deformation
327 v.w.	318 m	NB_2 deformation
362 w,p		CNB deformation
385 m,p	460 w	CNC deformation
	567 m	CNB deformation
586 s,p		B-B stretch
	608 m)	BN_2 deformation and B out of plane
	639 m)	
836 w	(830 w-m 832 ((839 w-m	B out of plane and mixed A' mode
895 m	892 m	NC stretch A''
973 m,p		NC stretch
	1049 m	CH_3 deformation
1066 m,dp.	1063 m	CH_3 deformation
	1101 w	Combination band ?
1110 w	1117 s	BN antisymmetric stretch
	1128 w)	CN stretch ? or combination bands.
1139 m,p	1140 w)	(2 x 567?)
	1186 m	CH_3 A'' deformation
	1216 s	CH_3 A' deformation

Table 22 - Continued.

Raman	Infra-red	Assignment
1342 m	1343 m	coupled vibration involving B-N stretch?
1376 s,p	1367 s	Symmetric BN coupled with symmetric CH_3
1414 s	1409 m	BN antisymmetric stretch
1447 s	1450 s	CH_3 A' rocking deformation.
	1502 s	
2795 s	2798 s	CH stretch
2850 s	2862 s	CH stretch
2872 s	2870 s	CH stretch
2928 s	2890 s	CH stretch
	2900, 2923	CH stretch
2983 m	2978 s	(2 x 1502) or CH stretch

Part 4: Solid Phase Spectrum of B_2Cl_4.

The reported change in structure for B_2Cl_4 on going from gas to solid phase was mentioned in earlier sections.

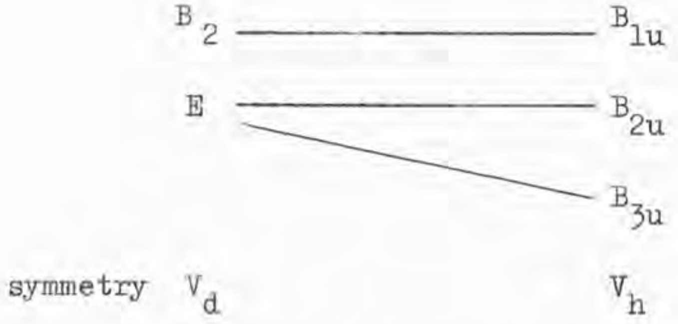
The selection rules for V_h and V_d symmetry are included in the appendix and the corresponding vibrations for a B_2X_4 molecule are shown below.

V_h: $3\ A_g + 2\ B_{2g} + B_g + A_u + 2\ B_{1u} + 2\ B_{2u} + B_{3u}$

V_d: $3\ A_1 + B_1 + 2\ B_2 + 3\ E$

For both structures there are therefore only five infra-red active vibrations, but there are six Raman active ones for V_h and nine for V_d symmetry. If it were possible therefore, an examination of the solid phase Raman spectrum would be extremely helpful. Solid phase Raman spectra are not easily obtained and for a molecule such as B_2Cl_4 which decomposes readily at 0^o and must be kept well below -100^o if it is to be studied in the solid phase, the experimental difficulties are indeed great. It is worth noting however that had a Raman spectrum been possible, an additional directive could have been obtained from the rule of mutual exclusion since the V_h structure has a centre of symmetry.

In studying the infra-red spectra alone it was realised that useful information would be restricted to changes in the location of fundamental frequencies and the ratios of peak intensities. Before discussing B_2Cl_4 it is useful to reflect upon the work of Gayles and Self[30] who studied the same structural changes in the related B_2F_4 molecule. Since constant reference will be made to the infra-red active vibrations for both point groups a correlation table for these modes is given below



In order to avoid confusion between the various symmetry designations of Mann and Fano for B_2Cl_4, Gayles and Self for B_2F_4, and the system suggested by Mulliken[72] and used in this work the following conversions are given

Mann and Fano	Mulliken	Gayles and Self
B_{1u}	B_{3u}	B_{2u}
B_{2u}	B_{2u}	B_{3u}
B_{3u}	B_{1u}	B_{1u}

It is not unreasonable to suppose that the intermolecular forces in solid B_2F_4 will be comparable to those in solid B_2Cl_4, and therefore, one might expect similar changes in the spectra, if both molecules undergo the same structural change when passing from gas to solid. Gayles and Self noted that the BF stretching vibration at c.a. 1150 cm.$^{-1}$ and the deformation vibration at c.a. 540 cm.$^{-1}$ of the E class underwent little changes in intensity with corresponding frequency shifts of about 1% to the red. The most spectacular change was found in the low frequency BF_2 deformation at 384 cm.$^{-1}$ which increases five-fold in intensity and shifts 17% to the blue. The antisymmetric BF stretching mode shifts by 3% to the red.

In B_2Cl_4 gas the corresponding vibrations are shown below with their B_2F_4 counterpart

B_2Cl_4[19]	B_2F_4	Class
730	1138	B_{1u}
291	537	
617	646	B_{3u}
917	1332	B_{2u}
180	383	

It was therefore expected that the largest shift (17%) would occur in the 180 cm.$^{-1}$ band (c.a. + 35 cm.$^{-1}$), followed by the 917 cm.$^{-1}$ band (c.a. -27 cm.$^{-1}$). Smaller shifts were expected for the other bands: c.a. - 11 cm.$^{-1}$ for the 617 cm.$^{-1}$ band, -10 cm.$^{-1}$ for the 730 cm.$^{-1}$ band and almost none for the 291 cm.$^{-1}$.

The low temperature spectra were run on the Unicam SP100 in the cell mentioned in Section 2, part 3. A great deal of difficulty was encountered in obtaining thin even films, and the spectra finally accepted were not as good as had been hoped for, especially in the 900 - 1000 cm.$^{-1}$ region where a number of peaks overlapped. The following points were noted however.

i) A band at approximately 715 cm.$^{-1}$ in the solid was split into four components: 691 cm.$^{-1}$ weak; 712 cm.$^{-1}$ strong; 722 cm.$^{-1}$ strong and 737 cm.$^{-1}$ weak. These bands must originate from the one found at 730 cm.$^{-1}$ in the gas. The shift of c.a. 15 cm.$^{-1}$ is in keeping with that expected for the change V_d — V_h.

ii) Bands observed at 610 and 380 cm.$^{-1}$ were too strong to measure accurately.

iii) A medium band at 521 cm.$^{-1}$ and a weak one at 458 cm.$^{-1}$ are assigned to combination and difference bands respectively by Mann and Fano. If the crystals of B_2Cl_4 were properly formed the low frequency band should not appear. It may be deduced therefore that either this is not a difference band or the B_2Cl_4 was improperly annealed.

iv) The B_{2u} band which should shift most was too low to be observed and the other B_{2u} band at 917 cm.$^{-1}$ was overlapped by other bands making it indistinct. It appeared however to be near 905 cm.$^{-1}$ in the solid.

It is not possible from the above data to conclude which structure prevails in the solid state but the few shifts observed are certainly in the right direction and of the order of magnitude expected for a change from V_d — V_h.

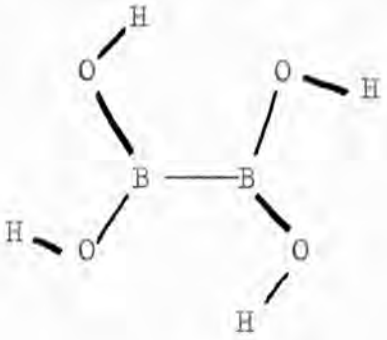
Part 5: The Infra-Red Spectrum of $B_2(OH)_4$.

As previously mentioned, Nikitin et al[29] have studied the infra-red spectrum of $B_2(OH)_4$, $B_2(OD)_4$ and $(BO)_x$. Their assignment of the bands was based upon a comparison of all three with boric acid and B_2Cl_4. A strong band observed at 1150 was assigned to the B-B stretch despite the fact that such a vibration is forbidden by the selection rules for a B_2X_4 molecule having any of the possible configurations. Because of this and the fact that in their spectra most of the bands overlapped and were complicated by the presence of mulling agents, it was decided to repeat the work.

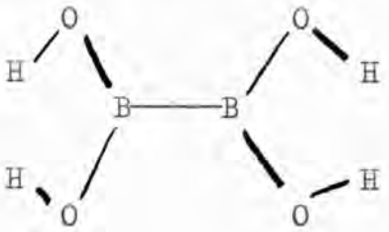
Spectra were run on the Unicam SP100 from 3500 down to 500 $cm.^{-1}$. $B_2(OH)_4$ was prepared and analysed as described later and samples of the order of 5 mg. were made up in KBr discs. The sample and reference wells of the spectrometer were evacuated. Spectra are given in figure 20.

If it is assumed that $B_2(OH)_4$, like crystalline B_2Cl_4 and B_2F_4 is planar, i.e. V_h symmetry, then there will be two infra-active BO stretching vibrations (B_{1u}, B_{2u}). These must be ascribed to the two strongest bands in the spectrum at 1325 and 1060 $cm.^{-1}$. In $B_2\left[OCH_3\right]_4$ B-O stretching vibrations are to be found at 1281 and 1104 $cm.^{-1}$ with the former band resulting from an antisymmetric vibration.[24] Nikitin et al have assigned the O-H stretching vibrations at 3230 and 3340 $cm.^{-1}$.

It now remains to assign the BO_2 deformation vibrations the BOH deformation and the $B\text{-}B(OH)_2$ vibration. This latter is attributed to the 584 $cm.^{-1}$ band since the corresponding vibration is to be found[24] at 578 cm.$^{-1}$ in $B_2(OCH_3)_4$ and in H_3BO_3 the E$'$ frequency occurs[89,90] at 544 cm.$^{-1}$, but drops to 525 cm.$^{-1}$ in $B(OCH_3)_3$.[91] The symmetry for the molecule is most probably C_{2h} but D_{2h} cannot be ruled out.



C_{2h}



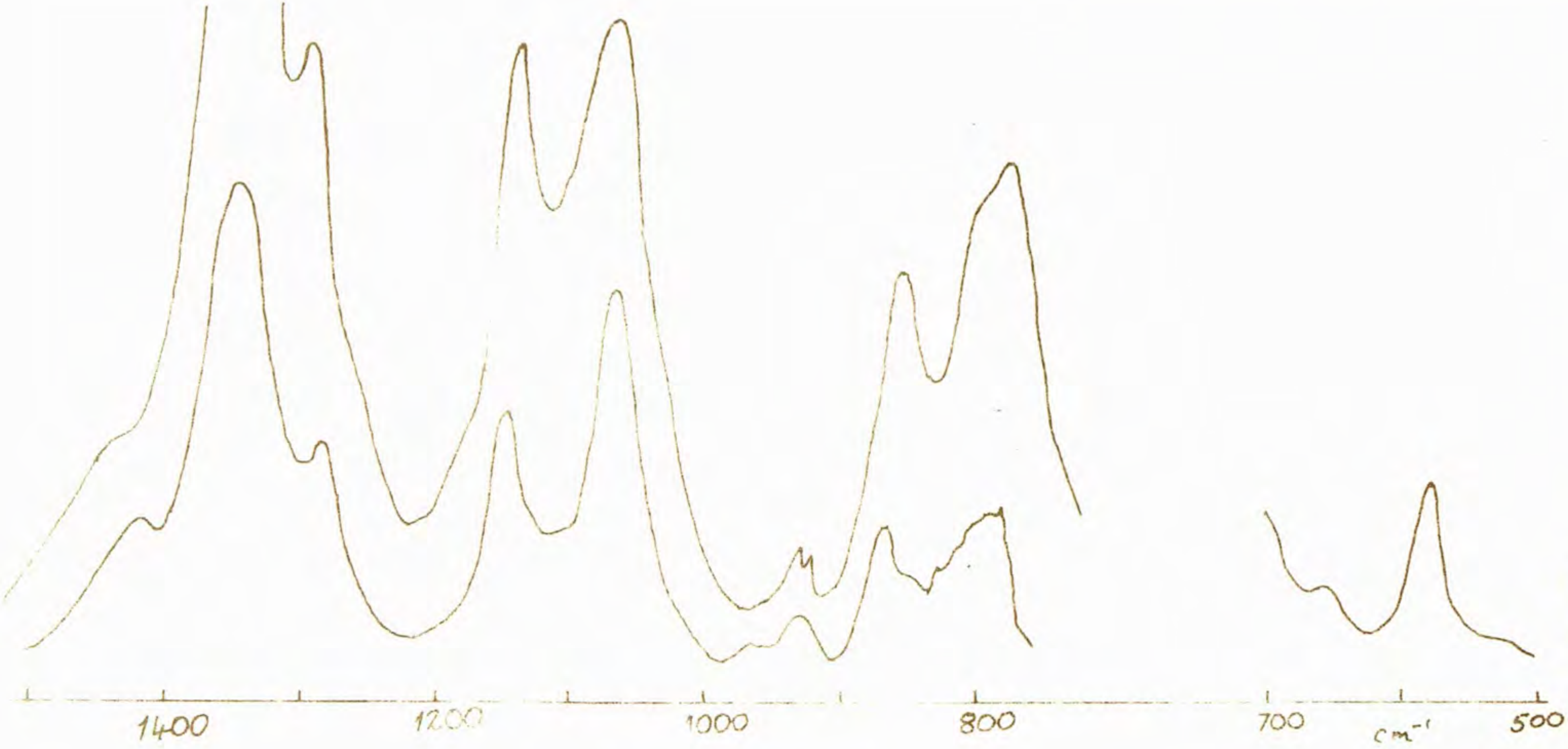
one of the possible D_{2h} structures.

In both cases however there are only two infra-red active BOH deformation vibrations (B_{1u} and B_{2u} for D_{2h}, and $2B_u$ for C_{2h}). In H_3BO_3 the E$'$ deformation is found[89,90] at 1183 cm.$^{-1}$ and the A$'$ at 1060 cm.$^{-1}$. It is possible that one of the BOH deformations is the 1150 cm.$^{-1}$ band but against this there is the fact that bands are observed near here in $B_2(OD)_4$ and $(BO)_x$.[29] On comparison with boric acid the other mode should belong, either to the band at 860 cm.$^{-1}$ or the one at 780, but since the out of plan $B\text{-}BO_2$ motion should occur near here also it is not possible to be sure on the basis of the present evidence.

The following table summarises the present assignment

FREQ. $CM.^{-1}$	ASSIGNMENT
3230	antisymmetric OH stretch
3250	symmetric OH stretch
1325	Antisymmetric BO stretch
1277	Combination band ?
1150	BOH deformation ?
1060	symmetric BO stretch
930	Combination band
860	) BOH deformation
780	) B out of plane
584	BO_2 deformation.

An attempt to obtain the Raman spectrum of an aqueous solution, in order to verify and perhaps add to the above table, was unsuccessful; the compound decomposing under the influence of the exciting radiation.



KBr DISCS of $B_2(OH)_4$

Fig. 20.

Part 6: The Infra-Red Spectra of BBr_3 and BI_3.

There have been numerous[1,28,27,92,93] studies of the vibrational spectra of the boron halides with particular reference to elucidating the force field[1,28,27,94,95] but for BBr_3 and BI_3 the measurements were all above 400 cm.$^{-1}$, [1,28]. For BBr_3 additional evidence was obtained from the Raman and a fairly good assignment was, therefore, possible[27,92,93]. The following work is mainly concerned with the low frequence (below 400 cm.$^{-1}$) modes in the infra-red. BI_3 was assigned by Wentink and Tiensuu[28] on the basis of one high frequency fundamental (ν_3) and a number of very weak combination bands. Because of the ease with which BI_3 decomposes at room temperature it was not possible for the above authors to study the Raman spectra using a conventional mercury source.

Results and Discussion.

The boron tri-bromide and iodide were obtained and for BBr_3 purified by methods to be described in a later section. The spectra of pure BBr_3 and solutions of BI_3 in benzene and carbon disulphide, were measured from 430-110 cm.$^{-1}$ on a far-infra grating spectrometer built in the department[69], and are shown in figures 21-23.

Boron Tri-bromide.

The D_{3h} point group is to be expected for both BBr_3 and BI_3 resulting in four fundamentals, A_1', A_2'' and $2E'$. The out of plane mode ν_2 (A_2'') shows an isotope split in BBr_3 of 18 cm.$^{-1}$ and the Redlich-Teller product ratio[31]

$$\frac{\nu(B^{10})}{\nu(B^{11})} \quad \text{is calculated at } 1.047$$

and is observed as 1.048. The shoulder on the in-plane deformation at 151 cm.$^{-1}$ might also be described as an isotope shift if it were not for the fact that the Redlich-Teller product ratio would be far too high. A more probable explanation is that it results from hot bands.

Although the A_1' stretching mode is forbidden it is not surprising that it is observed weakly at the thickness employed. The band observed at 301 cm.$^{-1}$ is readily explained as the first overtone of ν_4 with symmetry $A_1' + E'$. It might have increased its intensity as a result of Fermi resonance with ν_1.

<u>Boron Tri-iodide.</u>

Above 200 cm.$^{-1}$ there is little difference between the benzene and carbon disulphide solutions. No strong absorptions are found in this region even for a BI_3 to solvent ratio of 4:1 and at a 1 mm. path length. This implies that the umbrella mode ν_2 is weaker in BI_3 than BBr_3 because electrons are flowing into the boron p_z orbital, thereby making the iodine ~~fluorine~~ atom less negative and the change in bond dipole moment considerably smaller. One component of the 300 cm.$^{-1}$ complex is most probably the combination $\nu_1 + \nu_4$ (symmetry E'), the other cannot be explained as a combination band and must be assumed to be the ν_2 fundamental at 305 cm.$^{-1}$. This presents a problem however with some of the high frequency combination bands which were previously assigned[28] by assuming ν_2 to be at 336 cm.$^{-1}$. The 717 cm.$^{-1}$ can be assigned to $2\nu_2 + \nu_4$ (symmetry E') in resonance with ν_3 at 707 cm.$^{-1}$, but the origin of the 806 and 772 cm.$^{-1}$ bands are unknown. The 772 cm.$^{-1}$ band was observed in this work as a shoulder on the fundamental at 760 $cm.^{-1}$ but there was no trace of the 806 $cm.^{-1}$ band and since Wentink and Tiensuu only observed this peak in the vapour phase spectrum it most likely results from an impurity or decomposition product.

Below 200 $cm.^{-1}$ the spectra of CS_2 and benzene solutions are quite different. In particular the CS_2 solution only shows weak absorption for the forbidden A_1' fundamental ν_1 at 190 $cm.^{-1}$ but the benzene solution shows a strong absorption here. This is readily understood if the benzene is complexing ~~with~~ the BI_3 by π donation to the vacant p_z orbital on the boron atom, destroying the planarity of the BI_3. This would readily explain the fact that benzene solutions are BI_3 are almost colourless whereas it is impossible to obtain CS_2 solutions of BI_3 free of iodine. The 178 $cm.^{-1}$ band may be the first overtone of ν_4. Since ν_2 has been reassigned it was necessary to recalculate the corresponding force constant.

The G terms for the umbrella motion is:-

$G = 3\mu_I + 9\mu_B$ using standard notation.

(N.B. By using a slightly different definition for the internal co-ordinates Wentink and Tiensuu have $G = \mu_I + 3\mu_B$)

Hence $GF = (3\mu_I + 9\mu_B)\ f = \lambda_2$

where f is the force constant for the umbrella motion. f was found to be 0.065 md./Å compared with 0.079 md./Å calculated by Wentink and Tiensuu.

Tables 23 and 24 list the frequencies and assignments for both molecules.

Fig 21 BBr_3

fig 22

BI$_3$ in CS$_2$

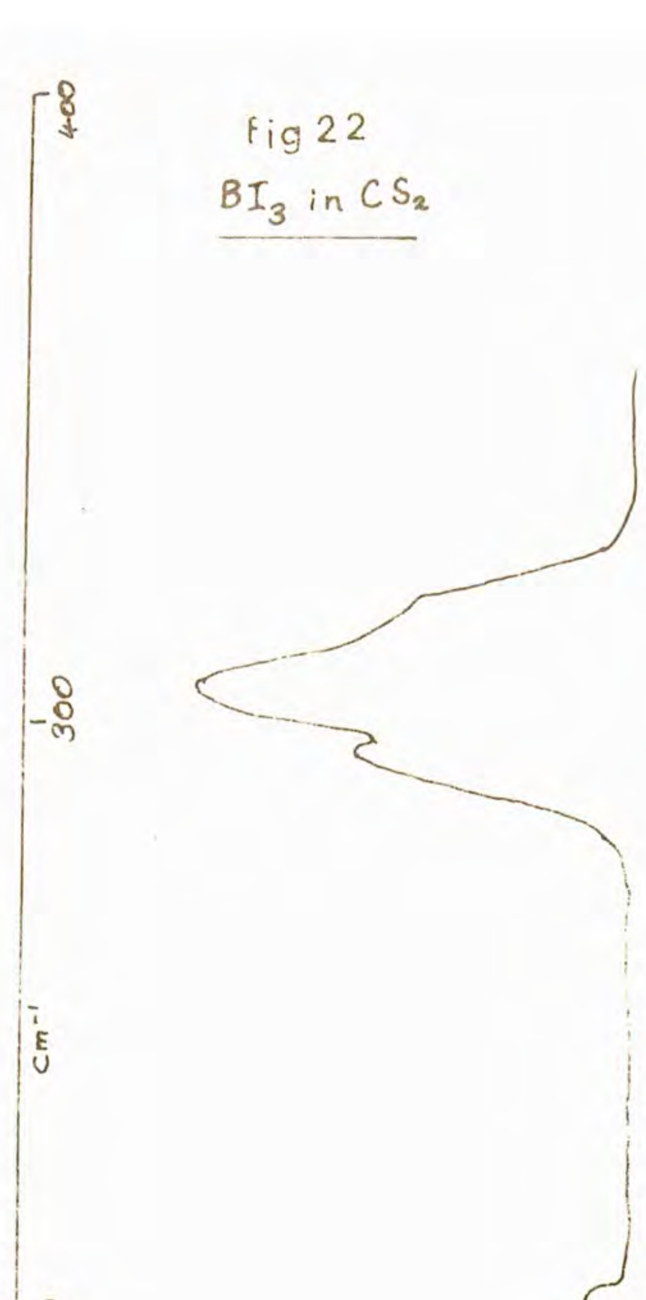
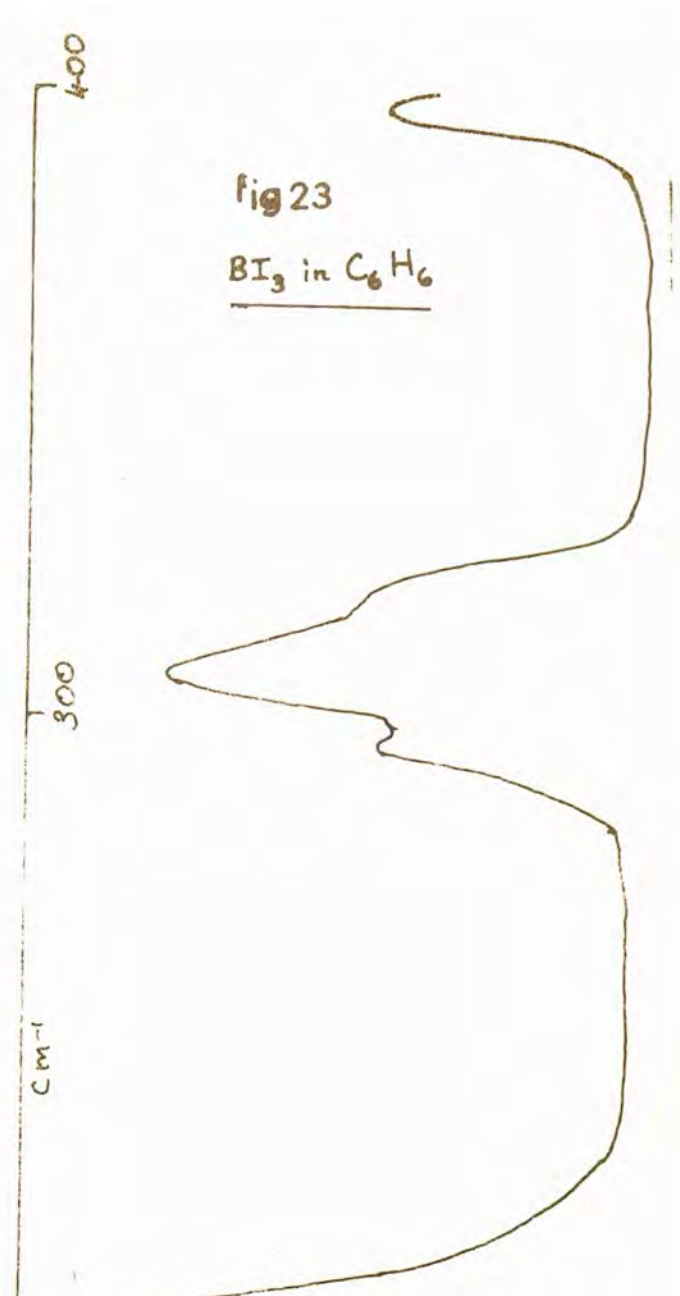


fig 23

BI$_3$ in C$_6$H$_6$



I.R. (a)	I.R.(b)	Raman (c)	Assignment
n.i. v.v.s.	845	846	ν_3 B^{10} E' stretch
n.i.	802	800	ν_3 B^{11}
429 m-w	430	-	$\nu_1 + \nu_4$
390 m-s	n.i.	-	ν_2 B^{10} A_2'' umbrella mode
372 s	n.i.	372	ν_2 B^{11}
301 w	n.i.		$2\nu_4$ $(A_1' + E')$
278 w	n.i.	279	ν_1 A_1' stretch
155 m.sh.	n.i.		$\nu_4 \rightarrow 2\nu_4$ "hot band"
151 s	n.i.	151	ν_4 E' deformation

n.i. - not investigated

(Frequencies in $cm.^{-1}$)

a - this work; b - Reference 28

c - References 27,92,93

VIBRATIONAL SPECTRA OF BBr_3

TABLE 23

CS_2 solution	benzene solution	Assignment
724 v.v.s.(a)		ν_3 B^{10}
692		ν_3 B^{11}
-	396 w	$\nu_2 + \nu_4$
320 w	320 w	ν_2 B^{10}
305 m	306 m	ν_2 B^{10}
295 w	294 w	$\nu_1 + \nu_4$?
206 v.w.		$2\nu_4$ B^{10} or $\nu_2 - \nu_4$
202 v.w.		$2\nu_4$ B^{11}
189 w	196 s	ν_1
	178 m.s.	$2\nu_4$?

(a) - Reference 28

Vibrational Spectra of BI_3

TABLE 24.

SECTION C.

EXPERIMENTAL

Part 1:

Introduction.

The compounds investigated fell, in general, into two main categories - those such as B_2Cl_4 and B_2F_4 that were very volatile and so sensitive to oxygen and moisture that they had to be handled in high vacua, and those compounds such as 2-chloro-1,3,2-dioxaborolan, and tetrakis (dimethylamino) diboron that could be handled in dry air or dry nitrogen. For the former, a complex vacuum line was built capable of retaining a vacuum of 10^{-6} mm. Hg., but the other compounds were either manipulated in a dry box or nitrogen filled dry-box or under a stream of dry nitrogen issuing from the mouth of a large funnel.

Reagents.

All the reagents used were thoroughly dried. Benzene, toluene, petroleum ether and ether were dried over sodium wire. Carbon disulphide was freed from sulphur by shaking with mercury and then dried over 4 A^o molecular sieves. Ethylene and propylene glycol were usually dried over anhydrous sodium sulphate and then purified by fractional distillation up an 18" column packed with glass helices and at 0.05 mm. Hg. When required ultra dry the following method was used[98]. Sodium sulphate-dried glycol was introduced into a round bottom flask fitted with a water cooled condenser and a calcium chloride tube at the outlet.

The apparatus was thoroughly dried beforehand by flaming with a bunsen burner. The temperature was then raised to just below reflux and small pieces of sodium (1 gm. for every 30 ml. glycol) dropped down the mouth of the condenser, and the mixture then refluxed for one hour. The apparatus was arranged to distill the glycol into a dry receiver and the middle cut collected.

Ethylene glycol $n_D^{25} = 1.4320$; Propane 1,3 diol $n_D^{25} = 1.4410$. (Reported[101]: $n_D^{20} = 1.4318$; and $n_D^{20} = 1.4396$)

2-chloro-ethanol (British Drug Houses) was dried over anhydrous sodium sulphate and fractionated up the glass helix column. The portion boiling at 128° was collected. $n_D^{25} = 1.4390$ (Reported[102] n_D^{25}=1.4401)

Boron trichloride was purified by multiple distillation in a high vacuum line through a trap at -45° into one at -95°, until the vapour pressure was 4 mm. at 0°. For the preparation of 2-chloro-1,3,2-dioxaborolan the commercial material (L. Light and Co.) was used without purification.

Boron tribromide (L. Light and Co.) was shaken with mercury and left for six hours to remove any bromine. The liquid was then poured into a dry nitrogen flushed round bottom flask fitted with the helix fractionating column and water cooled condenser. The portion boiling at 91° was collected and transferred to the vacuum line. Further purification was obtained by passing the vapour through a trap at 5° into one at -80°. The vapour pressure at 0° was found to be 18.5 mm.

Boron triiodide (L. Light and Co.) was not purified before use since it very readily decomposes. The commercial product was analysed and found suitable (Found: B, 2.49; I,96.6. Calc. for BI_3 : B,2·76 I, 97.2%).

Tetrakis (dimethylamino) diboron (Boron Consolidated U.K.) was distilled under reduced pressure (c.a. 14 mm.) up an 8" fractionating column packed with glass helices. The fraction boiling at 94° was collected.

Special Apparatus.

Detailed descriptions of the apparatus and conditions used in the preparation of 2-chloro-1,3,2-dioxaborolan and its -inan analogue were given in recent theses[14,100]. A slight modification was made for the distillation of the former compound in that the still head was constructed with a small water cooled condenser sealed in a vertical position between the Jackson condenser and the receiver arm.

The all glass vacuum line was built in accordance with the principles described by Sanderson[99] and is shown in the form of a block diagram in figure 24. The vacuum (10^{-6} mm. Hg., measured on a McLeod gauge) was obtained using a two stage Edwards oil-pump in conjunction with a three-stage water cooled mercury diffusion pump. Liquid air traps protected the pumps from harmful vapours. The line contained two main sections; one, grease free, in which all connections were made through glass seals and all taps were replaced by mercury filled Stock valves, and the other in which conventional high vacuum grease was employed (Edwards - Apiezon

M or N, or I.C.I. Fluorolube) for taps and joints. Compounds which were thermally sensitive, very volatile, or affected by the atmosphere were removed from and returned to the line in sealed ampules possessing a thin glass break-seal, others were transferred via a manifold. Fractionation was carried out by passing the vapours through U-tubes whose effective volumes had been increased by sealing glass thimbles to their base. The volume enclosed by a U-tube and its manometer was ascertained by comparing the pressure exerted in it by pure CO_2, with that in a standard vessel whose volume was known from an independent determination in which the quantity of water required to fill it was obtained by a double weighing. Pressures up to 700 mm. Hg. were measured on conventional mercury manometers.

Refractive Index.

These were measured on an Abbe' refractometer maintained at 25°.

Infra-red Spectrometers.

At the beginning of the work described herein only two spectrometers were available. One, a Perkin Elmer Infracord model 137 was only capable of medium resolution and was restricted to the 3500 - 650 $cm.^{-1}$ region. The other, a Hilger and Watts H800 could be used in the KBr region but it required long periods for temperature equilibration. Almost all the spectra in Section A were recorded on one of these instruments. When the work in Section A was begun two further instruments became available. One, a low frequency grating spectrometer could be used from 100 up to about 1400 $cm.^{-1}$. This instrument was built in the department[69]. The other spectrometer used was the Unicam SP100

Elemental Analysis.

Compounds containing boron and halogen which hydrolysed immediately and completely on immersion in water were analysed for hydrogen halide and boric acid by alkali titration.

In general hydrolysis occurs as follows:-

$$(RO)_2BCl + 3H_2O \longrightarrow HCl + 2ROH + H_3BO_3$$

The HCl would then be titrated with N/10 caustic soda using a methyl red indicator. Mannitol was then added and the boric acid mannitol complex titrated with N/10 caustic soda to a phenolphthalein end point. When BI_3 was analysed the method had to be modified because the small amounts of I_2 always present in this compound interfered with the end points. In this case the end points were obtained using a pH meter and titrating to pH 5 for HI and pH 9 for mannitol boric acid.

When the boron was not easily hydrolised to boric acid the compound was treated with a small quantity of concentrated nitric acid[14] and the mixture distilled with an excess of aqueous methanol. The trimethyl borate was collected under water and the solution analysed for boron as before.

A number of attempts were made to analyse $B_2(OH)_4$ using nitric acid to oxidise the diboron compound to boric acid[7]. The results, however, were not reproducible. On using 100 volume H_2O_2 as the oxidising agent reproducible results were obtained. Other elements were analysed for by A. Bernhardt, Max Planck Institute, Mulheim.

Compensation technique for Solvent Spectra.

When recording the spectrum of a compound in a solvent it is obviously desirable to obtain a trace free from solvent bands, and this becomes especially important when peak intensities of the solute are to be compared for solutions at different concentrations. This can only be done by placing sufficient solvent in the reference beam to cancel all peaks exactly.

First, the spectrum of the solvent was obtained at the path length to be used. The solution was then run over the same frequency range and those solvent absorptions of medium intensity which were well separated from solute ones were noted. With the solvent in a variable path length cell in the reference beam and the solution in the sample beam the spectrum was run over the regions of the recorded solvent peaks. By altering the path length of the solvent cell and re-running the spectrum it was usually possible to cancel out most solvent peaks. Sometimes, even with the best possible cancellation, the solvent peak could not be completely removed. In these cases a very shallow sine wave was obtained with the maximum and minimum displaced on either side of the original solvent peak. In the regions of strong solvent absorption the spectrum was unreliable because of the loss in energy. In order to verify that the cancellation was complete for bands in the region of the solute absorption the spectra were also run with slightly over and under compensating amounts of solvent. Any weak bands whose intensity showed considerable alteration in the expected sense were assumed to result from the solvent.

Part 2: Syntheses.

1). Preparation of 2-chloro-1,3,2-dioxaborolan or -inan.

The method used was essentially that described by Gerrard et al[12].

Boron trichloride was placed in a vessel of suitable size which had been previously cooled to -80° by a CO_2 acetone mixture and a -80° condenser attached. To the BCl_3 sufficient cooled dichloromethane was added to make a 50% solution. An equimolar quantity of ethylene glycol or propane-1,3-diol was added dropwise with constant stirring, the mixture being retained at -80°. The HCl evolved passed through the condenser and was either collected in a liquid air trap or absorbed in water via a non-suck-back device. After complete addition the mixture was allowed to warm up to room temperature to allow any dissolved HCl to come off. The HCl was then titrated with caustic soda and the titer used to calculate the percent reaction.

The reaction vessel was then fitted with the condenser head described earlier and evacuated to remove solvent, it was then placed in a heated oil bath, the Jackson filled with a mixture of solid CO_2 and acetone and the compound distilled out. Bath temperatures were usually between 100 and 160°. The 2-chloro-1,3,2-dioxaborolan distilled between 35 and 70° at 0.1 mm. Hg. The -inan analogue distilled between 20 and 22° at 0.1 mm. Hg.

Percent reactions were usually between 86 and 90%, but overall yields were never greater than 82%.

In the preparation of 2-chloro-4,5-tetradeutero-1,3,2-dioxaborolan the glycol (Merck Sharp Dohme, Montreal, Canada) was weighed first and an equimolar quantity of BCl_3 weighed out, using pipettes cooled to -80° by crushed CO_2, to obtain small amounts when necessary. In this reaction only 50% yield was obtained. The analysis was satisfactory (Found: B, 9.83; Cl, 31.7. Calc. for $D_4C_2O_2BCl$: B, 9.81; Cl, 32.14%).

2). Preparation of Tris (2-chloro-ethyl) borate.

2-chloro-ethanol (52.3 g.) was mixed with boric acid (14.0 g.) and benzene (50 ml.). Water produced in the reaction was removed by azeotropic distillation using a Dien and Starck apparatus. The benzene was removed on a vacuum pump and the borate ester distilled. The b.p. was 93.0° at 0.95 mm. Hg. $n_D^{25} = 1.4548$. (Found: B, 4.32. Calc. for $H_{12}C_6O_3Cl_3B$: B, 4.34%). Figure 25 shows the infra-red spectrum.

3). Preparation of 2-chloro-ethyl metaborate.

(a) From H_3BO_3 and $Cl(CH_2)_2OH$.

2-chloro-ethanol (26.84 g.) and boric acid (21.6 g.) were mixed with benzene (50 ml.) in a 250 ml. round bottomed flask. Azeotropic distillation in a Dean and Starck apparatus was used to remove the water produced on reaction. The hot liquid was filtered to remove any excess boric acid and the solvent removed on a vacuum pump. A yield of 87.5% was obtained. $n_D^{25} = 1.4655$. (Found: B, 8.05. Calc. for $H_4C_2O_2Cl\,B$; B, 10.18%).

(b) From B_2O_3 and $Cl(CH_2)_2O_3B$.

Tris (2-chloro-ethyl) borate (10.1 g.) was heated with boric oxide (3.0 g.) at 150° for 2 hours and stirred constantly. The mixture was allowed to cool and dichloro-methane added. The mixture was filtered and the solid freed from solvent by vacuum drying. A yield of 93% was obtained. (Found: B, 8.05%).

The mixture was repeatedly washed with 40-60° petroleum ether and again analysed. (Found: B, 10.0; H, 4.4; C, 21.4; Cl, 33.3: Calc. for $H_4C_2O_2ClB$: B, 10.2; H, 3.8; C, 22.6; Cl, 33.4%).

The spectrum showed the characteristic metaborate peaks[8] near 720 and 735 $cm.^{-1}$.

4). Preparation of B_2Cl_4.

The method used was essentially that described by Urry et al.[3]

BCl_3 was introduced into the vacuum line and purified by passing the vapour through a trap at 0°, to remove any silicon halides, into one at -95°. Any HCl was pumped off into a trap at -196° and discarded. Repeated purification gave a sample whose v.p. at -80° was 4.0 mm. The BCl_3 obtained was transferred to a separate section of the vacuum line which was divided into four parts, each isolated by mercury float valves. Each part contained two bulbs for holding BCl_3, a U-trap for carrying out fractionations and an 'H' shaped reaction vessel ('square four')[3] containing mercury pools in the lower limbs. Tungsten leads connected the mercury to a high voltage supply. Since B_2Cl_4 was known to decompose[23] readily at 0° the electric arc between the mercury pools was switched on and off every half minute using the circuit shown in Figure 26. BCl_3 was passed from a trap at -80^o through the electric arc into one at -196^o. In practice, it was usual to use two of the above 'H' vessels in parallel to increase yields.

When accumulation of B_2Cl_4 had lowered the v.p. of the boron trichloride the arcs were switched off, and the contents of each unit were fractionated through -80^o and -196^o traps. B_2Cl_4 collected in the one at -80^o whereas the BCl_3 passed into the other. Lower halides (B_4 Cl_4 etc.) were removed by passing the mixture through a series of traps at -63, -80 and -196^o. The pure B_2Cl_4 remained in the -80^o trap. The final sample had a v.p. of 46 mm. Hg. at 0^o and 10.7 mm. at -22.9^o. (Reported[3] values 44.5 and 10.7 mm. respectively).

5). Preparation of B_2F_4.

The method used in this preparation has been discussed in detail previously.[4]

In a typical synthesis SbF_3 (5 g.) and $SbCl_5$ (0.5 g.) were placed in a side arm of the reaction vessel which was connected to the vacuum line and then evacuated to 10^{-6} mm. Hg. A small plug of glass wool was placed in the tube connecting the vessel to the vacuum line to stop any SbF_3 from escaping into the manifold. The reaction system was isolated from the line by closing a mercury float valve and the antimony compounds sublimed from the side arm which was electrically heated into the reaction vessel cooled to -80^o.

B_2Cl_4 (1.684 m.mole) was condensed onto the SbF_3 at -196° and then allowed to warm up to -80° and then left for two hours. The contents of the vessel were then fractionated through traps at -80° and -196°. The -80° portion was returned to the reaction vessel and left in contact with the SbF_3 at -80° for a further three hours. The temperature of the reaction vessel was then allowed to warm up to room temperature. The complete reaction products were then repeatedly fractionated using traps at -80, -126 and -196°, only the -126° portion being used for the next pass. On the final pass the B_2F_4 exhibited the following v.p.

	(a)	(a)	(b)	(b)	(b)
Temperature °C	-80	-63.5	-52.3	-49.6	-47.0
Vapour Pressure mm.Hg.	15	87	206	241	269
Reported[4]	15	87.5	232	280	333

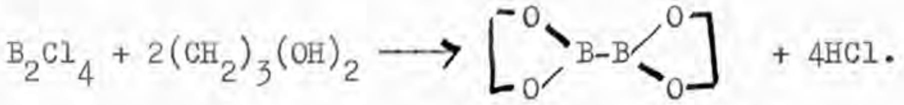
(a) solid; (b) liquid.

It would appear that some high molecular weight impurity was present but repeated fractionation did not improve the agreement. It is possible that one of the impurities found in the infra-red spectrum was F_2O produced by reaction of B_2F_4 with the glass[96] though this would not explain the low vapour pressure found after the fractionation.

6). Reaction between B_2Cl_4 and Propane-1,3-diol.

B_2Cl_4 (1.176 m.mole) was transferred in the vacuum line to a reaction vessel at -196° fitted with a magnetic stirrer and a manometer and containing propane-1,3-diol and an excess of pure dry CCl_4 as solvent.

On allowing the mixture to warm up to room temperature a reaction took place, a white solid was precipitated and a gas given off. The gas was passed through a trap at -80° into one at -196°, and then refractionated using traps at -111.9° and -196°. The -196° portion exhibited a v.p. of 124.3 mm.Hg. at -111.9° (reported[97] for HCl, 125 mm.Hg.). The HCl (4.24 m.mole) indicated a 90.1% reaction according to the following equation



After pumping off the solvent the solid was removed from the line under a N_2 atmosphere. It was very hydroscopic and soluble in benzene. Further examination was precluded by the lack of material.

7). <u>Reaction between sodium and 2-chloro-1,3,2-dioxaborolan.</u>

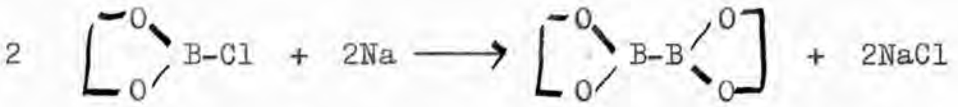
The following experiment was carried out in a dry box in an atmosphere of N_2.

Sodium (2 g.) was dissolved in liquid NH_3 (50 ml.) and toluene (100 ml.) was added. The solution was stirred constantly and allowed to warm up to room temperature. After 2 hours, when all the NH_3 had evaporated, a solution of 2-chloro-1,3,2-dioxaborolan (5.3 g.) in toluene (50 ml.) was added dropwise. The grey precipitate obtained was filtered from the solvent, washed with toluene and sucked dry on a filter pump. A portion of the solid which was removed from the dry box inflamed with water, but from another portion H_2 was collected. The aqueous solutions were strongly alkaline indicating the presence of unreacted Na in the precipitate. After neutralisation of the solution with HCl the addition of mannitol made it acid, and 3 ml. of caustic soda were required to neutralise it again. The presence of boron in the solid portion of the reaction product was confirmed by the flame test. The precipitate was not investigated further because of the difficulty of removing the Na.

The filtrate was removed from the dry-box in a sealed tube fitted with a side arm and tap. The tube was connected to an oil pump and the toluene sucked off. A white solid remained, a portion of which rapidly gained weight on standing in air. Furthermore, the solid did not readily go back into solution in toluene. Boron was indicated by the flame test.

A boron analysis was carried out by caustic soda mannitol titration. (Found: B, 9.62%).

Had the reaction gone according to the following equation



the boron content would have been much higher. In case all of the substance had not disproportionated to H_3BO_3 on dissolution in water a further analysis was carried out by the methanolic nitric acid distillation. (Found: B, 9.52. $H_8C_4O_4B_2$ Requires: B, 15.25%).

Qualitative elemental analysis was carried out by sodium fusion on two separate portions. Cl, and N were both absent. (B was also confirmed to be present).

The substance behaved like a plastic when under pressure. It began to soften at 90° but did not finally become liquid until 134°.

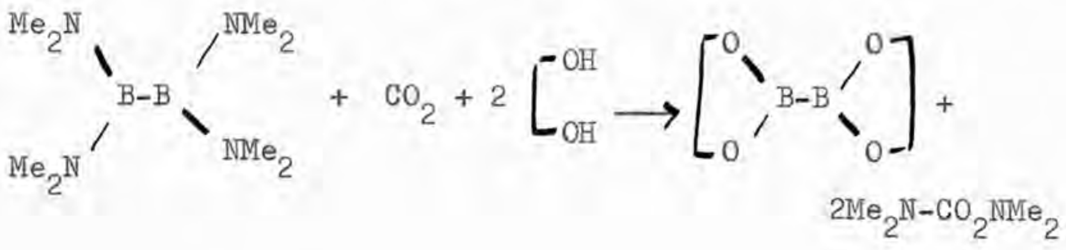
8). (a) Reaction of $B_2[N(CH_3)_2]_4$ with Ethylene Glycol and HCl

Tetrakis (dimethylamino) diboron (5 g.) was dissolved in ether (25 ml.) and an equimolar proportion of ethylene glycol added. Dry HCl, prepared from NH_4Cl and H_2SO_4, was bubbled in gently over a period of 2 hours with constant and vigorous stirring. A white precipitate separated which after removal of the solvent and ether washing, was shown to have reducing properties towards $AgNO_3$ and gave H_2 with dilute caustic soda.

The reaction products could not be separated either by solvent extraction with $CHCl_3$ or benzene or by vacuum sublimation.

(b) Reaction of $B_2[N(CH_3)_2]_4$ with Ethylene Glycol and CO_2.

Tetrakis (dimethylamino) diboron (3.9 g.) was poured into CO_2 saturated ether (25 ml.) containing ethylene glycol (2.5 g.). Sudden and exothermic reaction occurred in which a dense white precipitate was produced. The ether layer was separated from the solid by filtration and the ether removed on a water pump. A colourless oil remained which should have been dimethylamino-dimethylcarbamate had the reaction gone according to the following equation.



Carbamate synthesised independently by saturating dimethylamine with CO_2 was compared with the oil from the reaction.

i) Reaction product $n_D^{25} = 1.4590$ independent sample $n_D^{25} = 1.4525$. (Reported[103]: $n_D^{25} = 1.4512$).

ii) Infra-red spectra were identical.

iii) Both samples were subjected to thin layer chromatography on Al_2O_3 with a moving phase of butanol saturated with water and then developed with I_2. The Rf values were identical.

The solid product from the reaction was washed with ether and sucked dry on an oil pump. On warming to 100° in vacuo it slowly sublimed. This substance was soluble in water, produced H_2 with dilute NaOH and gave a silver mirror with aqueous $AgNO_3$.

A caustic soda mannitol titration was carried out. (Found: B, 8.40. ; $H_8C_4O_4B_2$ requires: B, 15.25%).

The analysis was repeated three times using a methanolic nitric acid distillation and the boron contents were found to be 4.4, 5.6 and 6.3%.

It is possible that some decomposition occurred during vacuum sublimation, but this was not verified.

9) <u>Preparation of Tetrahydroxy-diboron.</u>

$B_2[N(CH_3)_2]_4$ (21.84 g.) was added dropwise to an O_2 free ice slush mixture containing HCl (37 ml. concentrated HCl made up to 100 ml. and then frozen), the reaction being carried out in a stream of O_2 free N_2.

The solid precipitate was filtered off quickly and left in a vacuum desiccator for 24 hours to dry. (Found: B, 24.35. Calc. for $B_2O_4H_4$: B, 24.2%). A yield of 74% was obtained.

10). Reaction between 2-chloro-1,3,2-dioxaborolan I and Dimethyl formamide, II.

A small quantity of I was dropped into an excess of the amide II. A white precipitate formed immediately which was insoluble in benzene. The precipitate was filtered off and washed with benzene. The compound was analysed by dropping into water and analysing for HCl and H_3BO_3. (Found: B, 6.9 ; Cl 17.5. $H_{11}C_5O_3$ NCl B Requires: B, 6.1; Cl, 19.9%)

The sample of 2 (2'-chloroethyl) 1,3,2 dioxaborolan was kindly supplied by Dr. P.J. Gardner.

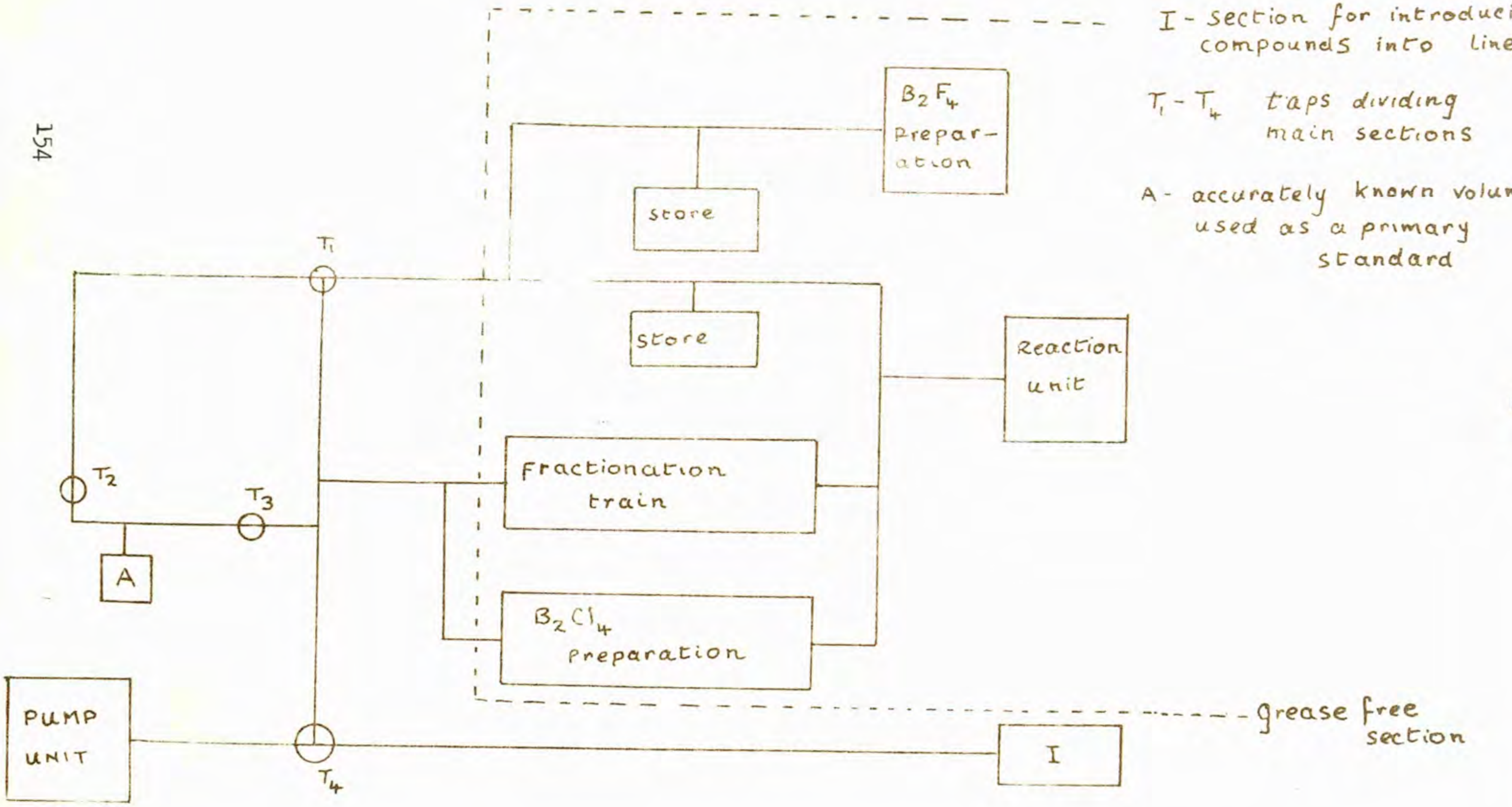

I - Section for introducing compounds into line
$T_1 - T_4$ taps dividing main sections
A - accurately known volume used as a primary standard
B_2F_4 Preparation
store
T_1
store
Reaction unit
T_2
T_3
Fractionation train
A
B_2Cl_4 Preparation
PUMP UNIT
T_4
I
grease free section

Fig.24.

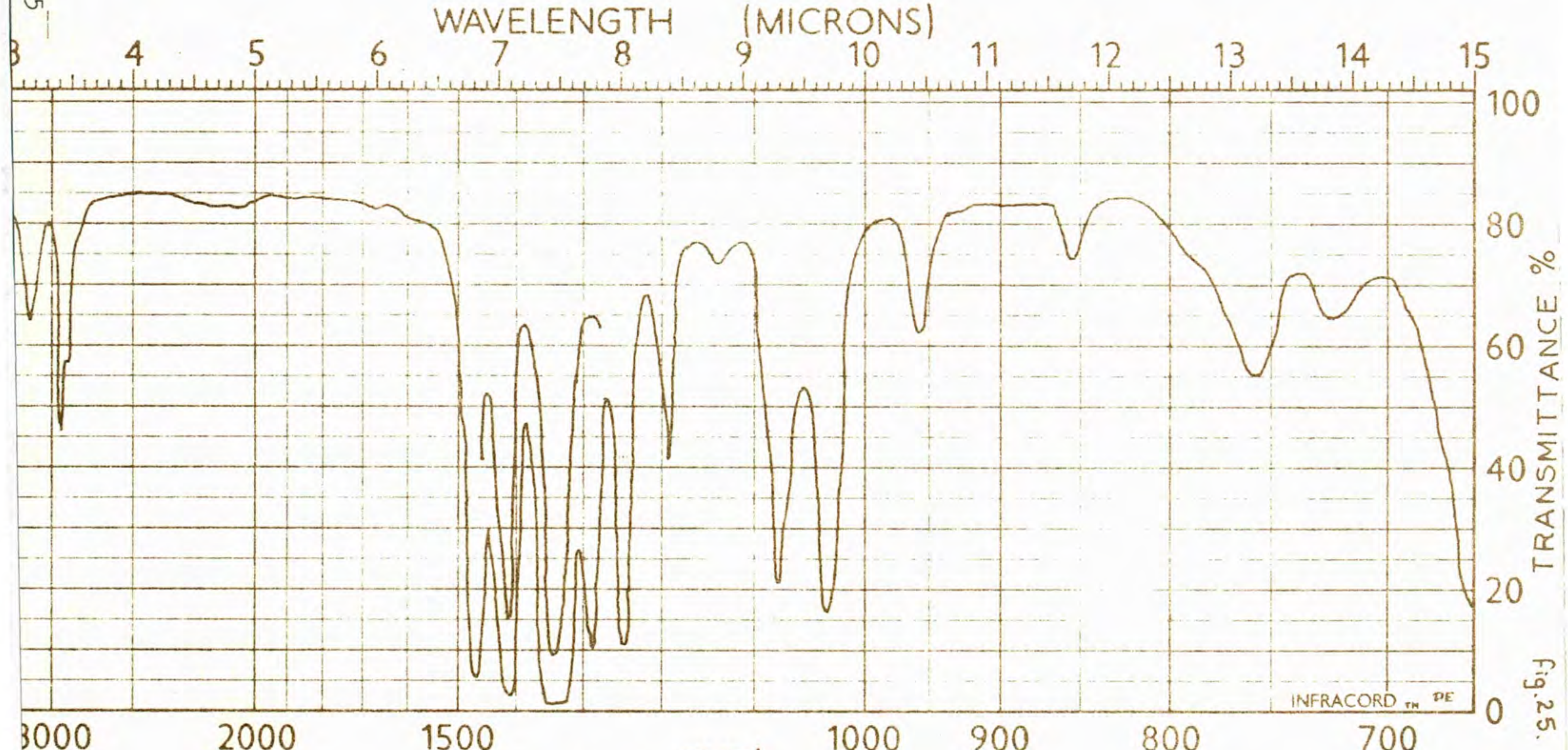


Fig.25.

$(Cl-(CH_2)_2-O)_3B$

R_1	25 Ω
R_2; R_3	220 K Ω
C	50µF, 50v
C_1	CAM FOR SWITCHING S_1
C_2	" " " S_2
N_1	NEON - MAINS ON
N_2	" - H.T. ON
L_1; L_2	24v, 0·3A BULBS
L_3-L_6	240v, 100WATT BULBS
S_1; S_2	MICRO SWITCHES
M	230v SYNCH. MOTOR 1 R.P.M
T_1	230v IN 20v OUT
T_2	230v IN 2000v OUT.

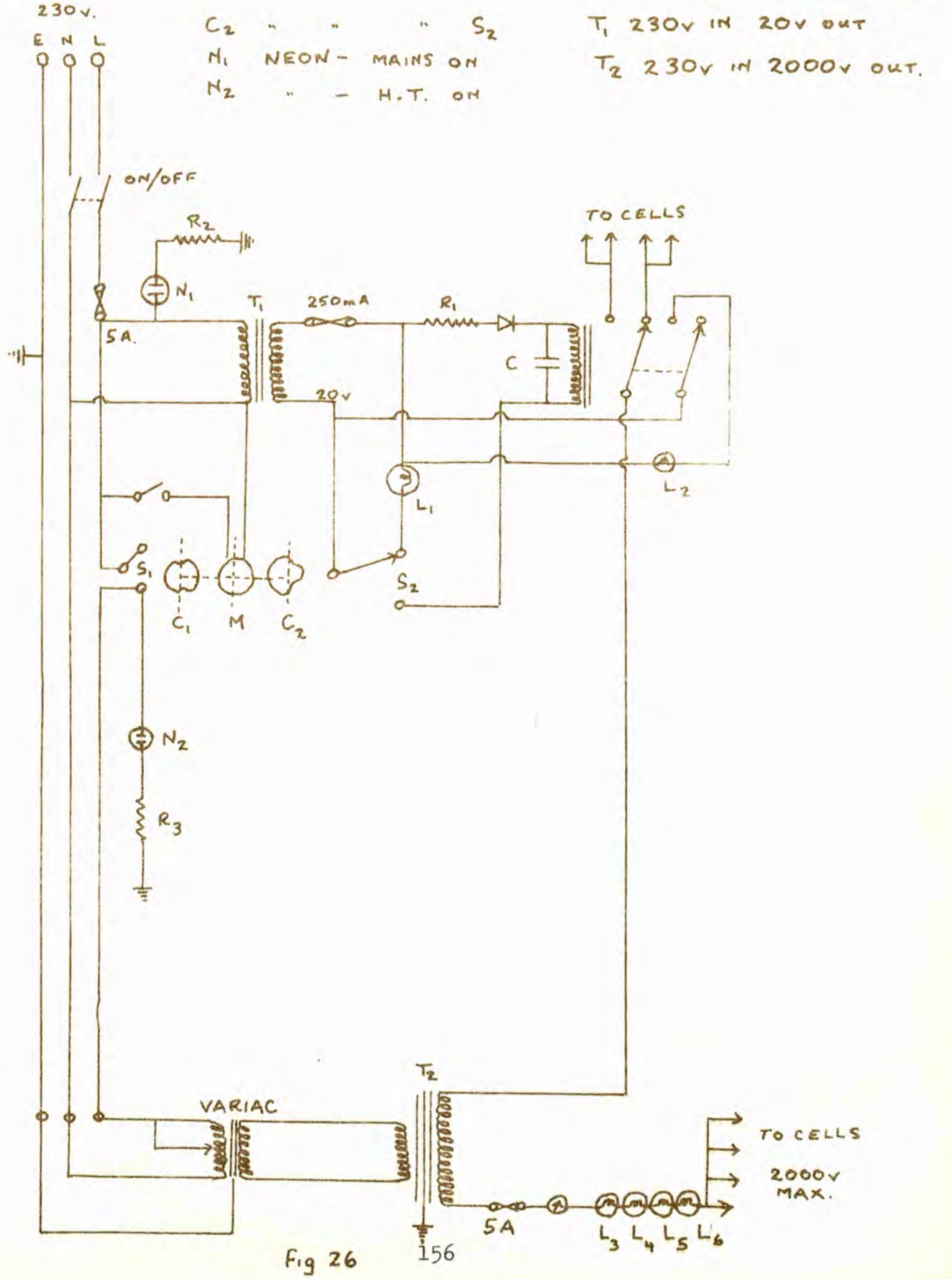


Fig 26

APPENDIX.

C_s	E	σ_h	
A'	1	1	T_x, T_y
A''	1	-1	T_z.

V_h	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(zx)$	$\sigma(yz)$.	
A_g	1	1	1	1	1	1	1	1	
B_{1g}	1	1	-1	-1	1	1	-1	-1	
B_{2g}	1	-1	1	-1	1	-1	1	-1	
B_{3g}	1	-1	-1	1	1	-1	-1	1	
A_u	1	1	1	1	-1	-1	-1	-1	
B_{1u}	1	1	-1	-1	-1	-1	1	1	T_z
B_{2u}	1	-1	1	-1	-1	1	-1	1	T_y
B_{3u}	1	-1	-1	1	-1	1	1	-1	T_x

V_d	E	$2S_4$	C_2	$2C_2'$	$2\sigma_d$	
A_1	1	1	1	1	1	
A_2	1	1	1	-1	-1	
B_1	1	-1	1	1	-1	
B_2	1	-1	1	-1	1	T_z
E	2	0	-2	0	0	T_x T_y

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GLOSSARY

Some of the Symbols Used.

V	Potential energy
T	Kinetic energy
f	Force constants
q	General displacement co-ordinate
R	Internal displacement co-ordinate matrix
G	Kinetic energy matrix
M	Mass Matrix
m_i	Mass of atom i
μ_i	$1/m_i$ or dipole moment depending upon the context
ν	Frequency in cm.$^{-1}$
ξ_i	One of the cartesian co-ordinates x, y or z.
ρ_α	A vector whose components are x, y, and z
$s_{t\alpha}$	Unit vector related to the internal displacement co-ordinates
U	Transformation matrix relating the symmetry co-ordinates to the internal displacement co-ordinates.
S	Symmetry co-ordinates or matrix of them.
χ	Character of a symmetry operation
γ	Symmetry class of some group
Γ	Irreducible representation of a group or the intensity of an absorption band depending upon the context.
$\mathcal{L}$	Transformation matrix relating the symmetry co-ordinates and normal co-ordinates with elements l.
Q	Normal co-ordinates
g	Order of a symmetry group.