

π -BONDING IN INORGANIC SYSTEMS

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ABSTRACT

Evidence from nuclear magnetic resonance studies for π -bonding between boron and nitrogen in the borazens is presented. Preliminary experiments, by infrared spectroscopy, which indicate that a similar situation might exist between phosphorus (III) and nitrogen, in open chain compounds, are also reported.

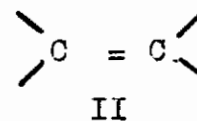
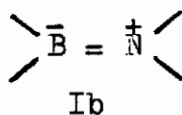
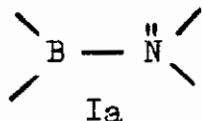
The energy barrier to rotation about the BN bond in dimethylaminophenylchloroborane is calculated (from four different observations on the N.M.R. spectra) as 18 ± 2 kcals.

Exploratory measurements on certain boron-oxygen compounds are also presented.

INTRODUCTION

It has been suggested that the search for monomers, suitable as intermediates in the synthesis of inorganic polymers, might well be pursued among those inorganic compounds in which a high degree of π -bonding occurs.

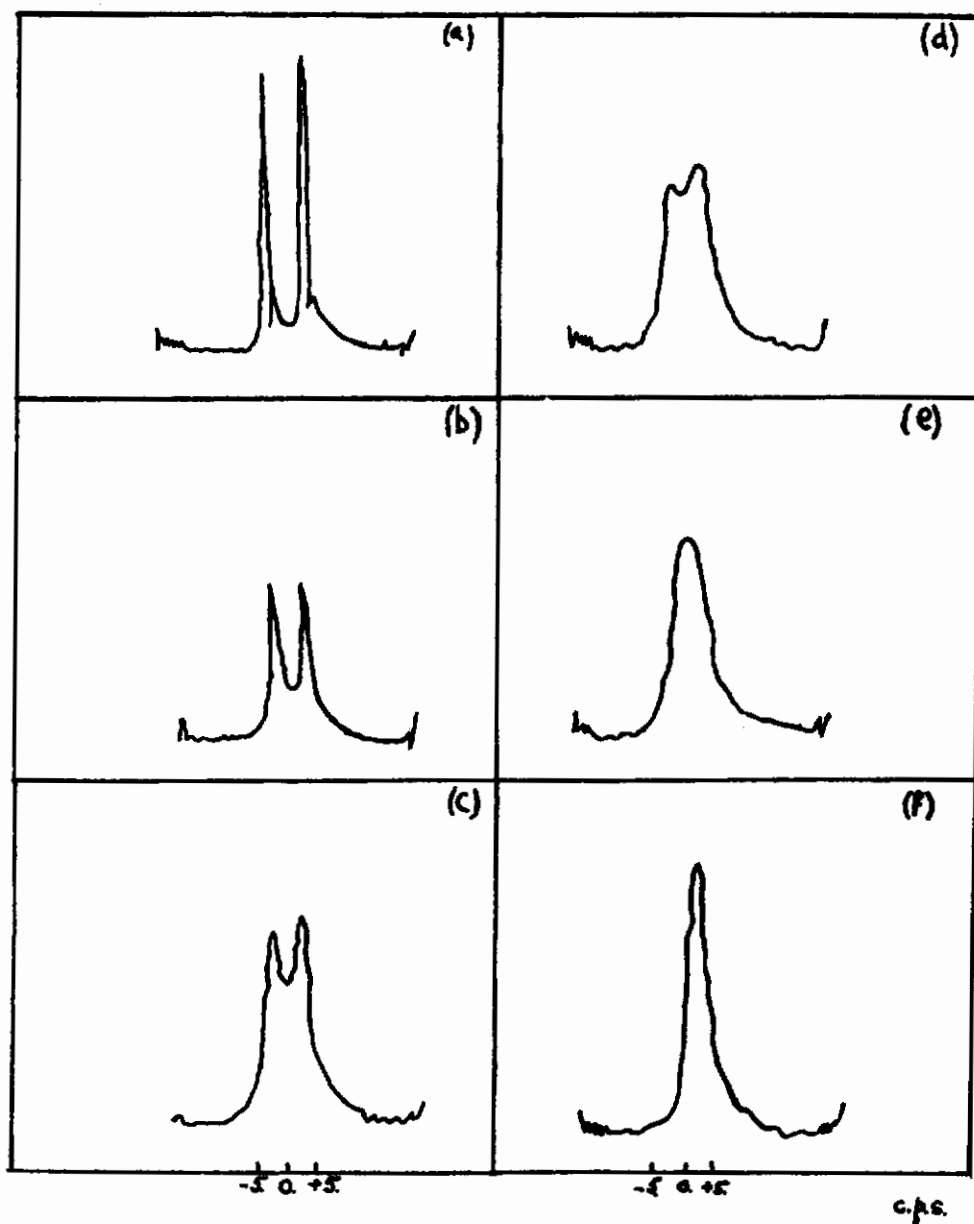
The borazens, (I), i.e. open-chain compounds in which both boron and nitrogen are three co-ordinate, are isoelectronic and isosteric with the corresponding olefins, (II). This point is particularly emphasized by the canonical form (Ib).



Much circumstantial experimental evidence for the occurrence of π -bonding in the borazens is available (see ref.1. and references cited therein) and it seemed likely that more direct evidence for the phenomenon could be obtained from nuclear magnetic resonance data and especially from studies on energy barriers to rotation.

Results of ^1H nuclear magnetic resonance experiments on methylphenylaminodimethylborane,² $\text{C}_6\text{H}_5\text{NCH}_3\text{B}(\text{CH}_3)_2$, and phenyldimethylaminochloroborane,³ $\text{C}_6\text{H}_5\text{BClN}(\text{CH}_3)_2$, have been

DIAGRAM 1



^1H SPECTRA OF PHENYLDIMETHYLAMINOCHLOROBORANE AT SEVERAL TEMPERATURES (a) 23°, (b) 93°, (c) 103°, (d) 109°, (e) 118°, (f) 137°.

SPECTRA WERE RECORDED AT 40 Mc/Sec., ABSORPTION OCCURRED AT $\gamma_{1/2}$

published. These results confirm that a high barrier to rotation (estimated at 15 ± 3 kcal in the former and 18 ± 2 kcal in the latter) exists between boron and nitrogen and we³ have shown in a preliminary way, by comparing $\text{PhB}(\text{Cl})\text{NMe}_2$ and $\text{PhB}(\text{NMe}_2)_2$, that the high barrier in the former is essentially due to π -bonding and not to steric considerations. Our evidence will be elaborated upon in this paper.

DISCUSSION

1. THE BORON-NITROGEN SYSTEM

In the borazens a "partial" double bond, due to delocalisation of p_π -type nitrogen electrons into a vacant p_π -type boron orbital, is to be expected.

The ^1H nuclear magnetic resonance spectrum of the compound phenyldimethylaminochloroborane, $\text{C}_6\text{H}_5\text{BClNMe}_2$ (I), examined at 40 Mc/sec, showed a doublet at $\tau \approx 7.2$ (fig. 1a.) attributed to methyl absorption, the occurrence of a doublet being consistent with the presence of two sets of protons in chemically-different and equally-abundant environments (cis- or trans- to the phenyl group). At progressively higher temperatures band broadening and decrease of maxima separation were observed (fig. 1b - 1d.), and at about 118° the doublet structure collapsed into a single broad band. At still higher temperatures the single band became increasingly narrow (fig. 1e, 1f.). The association of this kind of spectral behaviour with variable isomeric inter-conversion is well-established.⁴

From observations on the recorded spectra, a value of 18 ± 2 kcal has been calculated for the energy barrier to rotation about the BN bond.

The ^1H nuclear magnetic resonance spectrum of bis-(N,N-dimethylamino)phenylborane, $\text{C}_6\text{H}_5\text{B}(\text{NMe}_2)_2$ (II), showed no splitting of the methyl absorption at room temperature and this is taken to indicate that the energy barrier to rotation about the BN bond in this compound is rather low, probably less than 10 kcal. Similar observations were also made on bis(N-methylamino)phenylborane, $\text{C}_6\text{H}_5\text{B}(\text{NHMe})_2$ (III).

Steric effects with respect to rotation about the BN bond would undoubtedly be greater in compound (II) (and III) than in (I). The presence of a lower barrier in (II), where back donation from two nitrogen atoms can occur, proves that the restriction to rotation in (I), where the boron atom is linked to a single nitrogen, must be due to electronic effects (i.e. π -bonding) rather than to steric factors. Furthermore these

TABLE 1.

| Compound | B.P. °C/mm. | n_D^{20} | Method of Synthesis | Ref. |
|------------------------------------------|----------------|------------|----------------------------------------------------------------------------------------------------------------------------------|------|
| I. PhBClNMe ₂ | 75/2 | 1.53202 | PhBCl ₂ + Me ₂ NH $\xrightarrow{Et_3N}$ PhBClNMe ₂ + Et ₃ N.HCl | 10 |
| II. PhB(NMe ₂) ₂ | 60/0.4 | 1.51684 | PhBCl ₂ + 4Me ₂ NH $\xrightarrow{-78^\circ}$ PhB(NMe ₂) ₂ + 2Me ₂ NH.HCl | - |
| III. PhB(NHMe) ₂ | 86/3 | 1.52902 | PhBCl ₂ + 4MeNH ₂ $\xrightarrow{-78^\circ}$ PhB(NHMe) ₂ + 2MeNH ₂ .HCl | - |
| IV. Ph.BClNMePh | 102/0.2 | 1.58774 | PhBCl ₂ + PhNMeH $\xrightarrow{Et_3N}$ PhBClNMePh + Et ₃ N.HCl | 10 |
| V. PhBClNMe ⁱ Pr | 90/2 | 1.51932 | PhBCl ₂ + MeNH ⁱ Pr $\xrightarrow{Et_3N}$ PhBClNMe ⁱ Pr + Et ₃ N.HCl | - |
| VI. PhBClNMeEt | 82/0.2 | 1.52844 | PhBCl ₂ + MeNH ⁱ Et $\xrightarrow{Et_3N}$ PhBClNMeEt + Et ₃ N.HCl | - |
| VII. PhBBrNMe ₂ * | 63/0.8 | | PhBBr ₂ + PhB(NMe ₂) ₂ → 2PhBBrNMe ₂ . | - |
| VIII. PhBFNMe ₂ * | 62/3 | 1.50581 | 3PhBClNMe ₂ + SbF ₃ → 3PhBFNMe ₂ + SbCl ₃ . | - |
| IX. PhBClOMe* | 57/5 | 1.51110 | PhBCl ₂ + PhB(OMe) ₂ → 2PhBClOMe | 11 |
| X. PhB(OMe) ₂ | 46/3 | 1.49599 | PhBCl ₂ + 2MeOH $\xrightarrow{O^\circ}$ PhB(OMe) ₂ + 2HCl | 11 |
| XI. PhPClNMe ₂ | 80/0.1 | 1.57530 | PhPCl ₂ + Me ₂ NH $\xrightarrow{Et_3N}$ PhPClNMe ₂ + Et ₃ N.HCl | - |
| XII. PhP(NMe ₂) ₂ | 58/0.1 | 1.54791 | PhPCl ₂ + 4Me ₂ NH → PhP(NMe ₂) ₂ + 2Me ₂ NH.HCl | - |

* Not yet completely analysed.

results show that cis/trans isomerism due to restricted rotation about inorganic atomic pairs, can be extended beyond the only hitherto established case of $-N=N-$.

Further investigations into the borazen system have been based upon the compounds IV - VIII (Table 1). The spectrum of compound IV, methylphenylaminophenylchloroborane, $C_6H_5BCl(CH_3NC_6H_5)$, showed no splitting of the methyl resonance in the range 25 - 200°, and this may be due to a high barrier to rotation about the BN bond, mainly for steric reasons, and a steric preference for the less hindered isomer. Likewise, aryl-substituted amides (e.g. N-methylacetanilide) show a single methyl resonance whereas N,N-dimethylamides show a doublet, and it has been suggested⁵ that at least 10% of the less-favoured isomer is required to give a recognisable signal. Chemical and spectroscopic evidence for steric hindrance in the borazens, particularly in the N-aryl derivatives, is available.¹

The spectra of the remaining compounds have only recently been recorded.

2. THE BORON-OXYGEN SYSTEM

Thermochemical^{6a} and spectroscopic^{1,6b} evidence shows that although a B-O bond has some double bond character, the ability to form π -bonds with boron is greater for nitrogen than oxygen.

In order to investigate this further we have synthesised samples of the esters chloromethoxyphenylborane, $C_6H_5BCl(OMe)$, (IX), and dimethoxyphenylborane, $C_6H_5B(OMe)_2$, (X).

The ¹H^{nuclear} magnetic resonance spectrum of these compounds recorded at 60 Mc/sec (room temperature) reveals, in both cases, a broad low field signal characteristic of the phenyl group, together with a single line at somewhat higher field which is attributable to the methyl group resonance.

This section of the work is being continued.

3. THE PHOSPHORUS(III)-NITROGEN SYSTEM

π -Bonding in the phosphorus nitrogen bond has been invoked in the discussion of a PN compound and its suggested pseudoaromaticity.⁷ Spectroscopic investigations into the three co-ordinate phosphorus nitrogen system have therefore been undertaken.

The infrared spectrum of N,N-dimethyl-P-phenylphosphonamidous chloride, $C_6H_5PClNMe_2$, (XI), shows a medium band in the 1600 cm^{-1} region, characteristic of monosubstituted aromatic compounds. This is accompanied by another band at approximately 20 cm^{-1} lower and this may be due to the presence of an

unsaturated side chain which allows extended conjugation with the aromatic ring. Similar features have been observed in the spectra of borazens.¹ It is significant that the low intensity band is absent in N,N,N',N'-tetramethyl-P-phenylphosphonous diamide, $C_6H_5P(NMe_2)_2$, (XII), where the extent of π -bonding would be expected to be reduced.

The 1H nuclear magnetic resonance spectra of these compounds recorded at 60 Mc/sec, are both characterised by a broad low field band, attributed to phenyl group resonance, and a doublet at higher field. This doublet was shown to arise from spin-spin interaction between the phosphorus and hydrogen nuclei by measurements at 25 Mc/sec.

SYNTHESIS OF MODEL COMPOUNDS

The compounds which have been prepared for use in these investigations, are listed in Table 1. Methods used for their synthesis are also indicated in the Table.

All the compounds, except for the dimethylaminohalogenophenylboranes, (VII) - (IX), were fully characterised by elemental analyses.

PHYSICAL MEASUREMENTS

Infrared spectra were recorded on a Perkin Elmer Model 21 (Sodium Chloride optics) and on a P.E. Model K14 (potassium bromide optics). Samples were studied as pure materials. Compounds (I) - (VIII) were each characterised by having a strong absorption band in the range 1450 ± 100 cm^{-1} , which may be attributed to the BN stretching frequency.¹ Comparison of the spectra of the phosphorus compounds (XI) and (XII) with their boron analogues (I) and (II) confirms this assignment and moreover reveals that the PN stretching vibrations fall at 986 cm^{-1} for $PhPClNMe_2$ and at 971 cm^{-1} (asymmetric) and 957 cm^{-1} (symmetric) for $PhP(NMe_2)_2$.

Nuclear magnetic resonance spectra were recorded on a Varian Associates Model V4300B equipped with variable temperature probe or on an A.E.I. RS2 spectrometer. Spectra were recorded at 60, 40, and 25 Mc/sec.

Mathematical calculations were carried out on the Ferranti Mercury computer in the Department of Electrical Engineering, University of Manchester.

RESULTS

AND

Mathematical Approach to the Calculation of Barriers to Internal Rotation.

A quantitative treatment for the study of internal rotation in molecules by nuclear magnetic resonance has been developed, by suitable modification of the Bloch equations to take into account exchange between two equally abundant sites with equal transverse relaxation times (T_2). The most general treatment is that of McConnell⁸, who has shown that the total r.f. magnetisation in such a system is given by

$$G = \frac{i w_1 M_z \tau \left\{ 2 + \left[\frac{1}{T_2} - i(\Delta w_A + \Delta w_B) / 2 \right] \tau \right\}}{\tau^2 \left(\frac{1}{T_2} - i \Delta w_A \right) \left(\frac{1}{T_2} - i \Delta w_B \right) - 1}.$$

where M_z = total magnetisation

T_2 = Transverse Relaxation Time (assumed equal for the two environments)

τ = Mean lifetimes of environments A and B

$$\frac{1}{\tau_2} = \frac{1}{T_2} + \frac{1}{\tau}$$

$$\Delta w_A = w_{OA} - w.$$

w_{OA} = Larmor Precession angular velocity of nuclei in environment A in the STATIC field only.

w = Angular velocity of the rotating magnetic field, H_1 .

$$w_1 = \gamma H_1$$

γ = Magnetogyric Ratio

If the internal chemical shift $w_{OA} - w_{OB} = \delta w$, and the separation of the angular velocity, w , from the mean shift

$$\frac{w_{OA} - w_{OB}}{2} - w = \Delta w$$

Then:

$$\Delta w_A + \Delta w_B = 2 \Delta w.$$

$$\Delta w_A - \Delta w_B = \delta w$$

$$\Delta w_A = \Delta w + \delta w / 2.$$

$$\Delta w_B = \Delta w - \delta w / 2.$$

$$\text{and } G = \frac{i w_1 M_z \tau (2 + \tau/T_2 - i \Delta w \tau)}{[1 + \tau(1/T_2 - i \Delta w - i \delta w/2)][1 + \tau(1/T_2 - i \Delta w + i \delta w/2)] - 1}.$$

An expression for the out of phase component of the r.f. magnetisation v , which is proportional to the intensity of absorption, can be obtained from the imaginary part of this expression for G .

$$v = \frac{w_1 M_z [(1 + \tau/2T_2)P + \tau/2(\Delta w)^2(1 + \tau/T_2)]}{P^2 + (\Delta w)^2(1 + \tau/T_2)^2}.$$

$$P = \tau/2 [(1/T_2)^2 - \Delta w^2 + (\delta w/2)^2] + 1/T_2$$

Differentiation of this expression to obtain extreme values of v , yields a fifth order equation in $(\Delta w)^5$

$$\frac{\tau^4}{T_2} (\Delta w)^5 + 8 \tau^2 S (1 + \frac{\tau}{2T_2}) (\Delta w)^3 + 16 \left[\left(1 + \frac{\tau}{2T_2}\right)^2 1 + \frac{1}{T_2} - \frac{\tau S}{2} \left(2 + \frac{3\tau}{2T_2}\right) \right] S \Delta w = 0$$

$$S = 1/T_2 + \tau/2T_2^2 + \tau/2 (\delta w/2)^2$$

The solutions to this equation are at $\Delta w = 0$, or

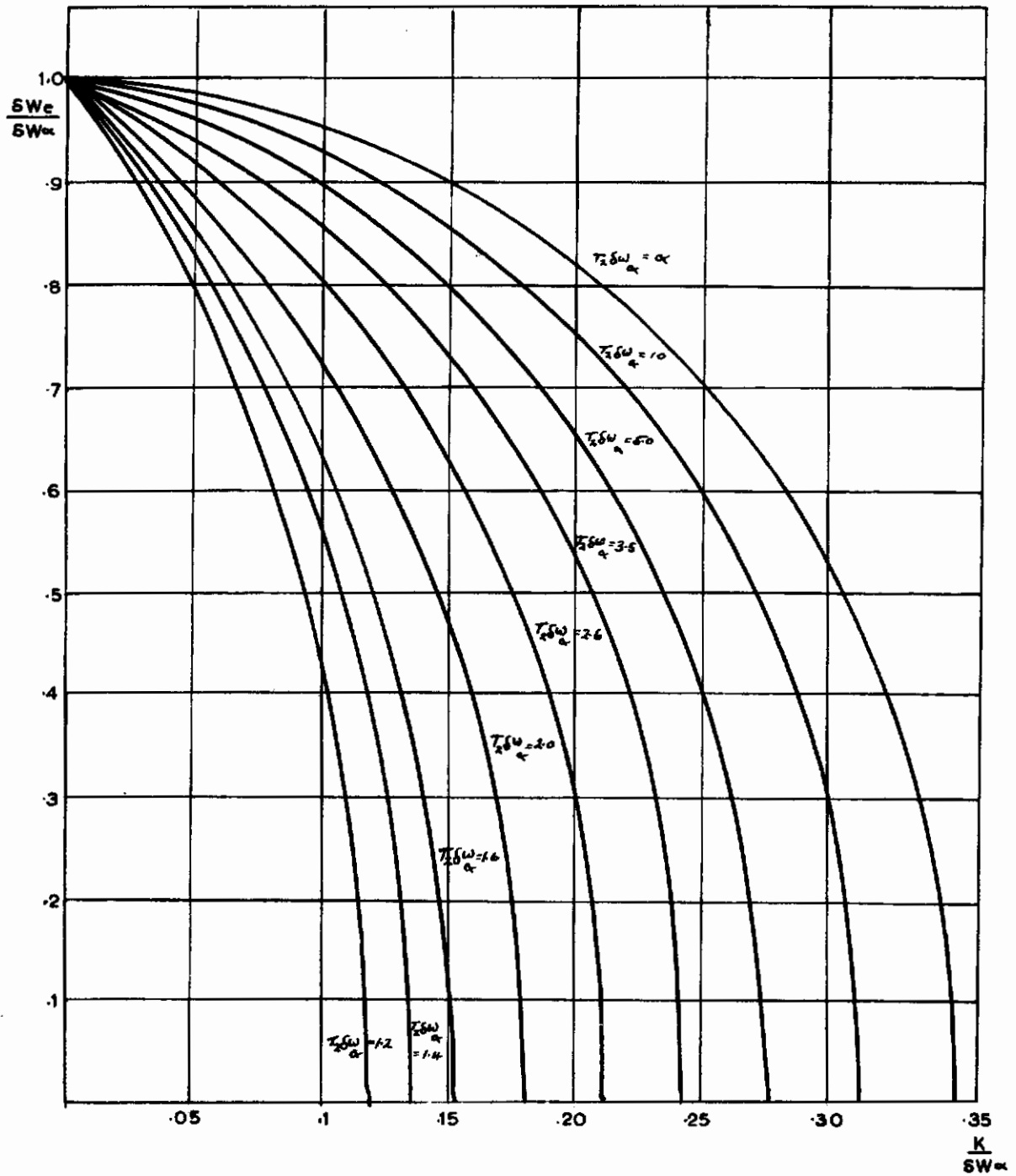
$$\Delta w = \pm \left[-2S \left(\frac{1}{\tau} + \frac{2T_2}{\tau^2} \pm S^{\frac{1}{2}} (\delta w) \frac{2T_2^2}{\tau^3} + \frac{4T_2}{\tau^2} + \frac{2}{\tau} \right)^{\frac{1}{2}} \right]^{\frac{1}{2}}$$

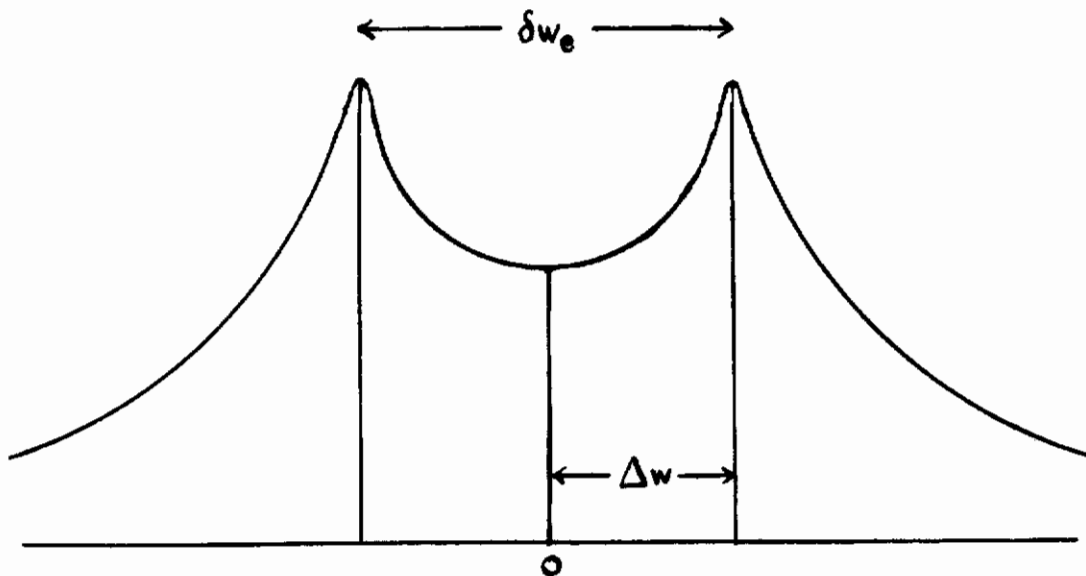
The negative possibility in the second choice of signs may be disregarded since this will lead to complex roots.

If the second term of this expression is ^{numerically} greater than the first, then the resultant two real roots will give an expression for the two maxima which will occur at positions Δw from a zero line and be given by

$$\Delta w = \pm \left[-2S \left(\frac{1}{\tau} + \frac{2T_2}{\tau^2} \right) + S^{\frac{1}{2}} (\delta w) \left(\frac{2T_2^2}{\tau^3} + \frac{4T_2}{\tau^2} + \frac{2}{\tau} \right)^{\frac{1}{2}} \right]^{\frac{1}{2}}$$

DIAGRAM 2





The observed separation of the two peaks $\delta w_e = 2|\Delta w|$

$$\delta w_e = 2 \left[-2S \left(\frac{1}{\tau} + \frac{2T_2}{\tau^2} \right) + S^{\frac{1}{2}}(\delta w) \left(\frac{2T_2^2}{\tau^3} + \frac{4T_2}{\tau^2} + \frac{2}{\tau} \right)^{\frac{1}{2}} \right]^{\frac{1}{2}}$$

$$\text{Hence } \frac{\delta w_e}{\delta w} = 2 \left[-2 \left(\frac{1}{T_2 \delta w} + \frac{\tau \delta w}{2(T_2 \delta w)^2} + \frac{\tau \delta w}{8} \right) \left(\frac{1}{\tau \delta w} + \frac{2T_2 \delta w}{(\tau \delta w)^2} \right) + \left(\frac{1}{T_2 \delta w} + \frac{\tau \delta w}{2(T_2 \delta w)^2} + \frac{\tau \delta w}{8} \right)^{\frac{1}{2}} \left(\frac{2(T_2 \delta w)^2}{(\tau \delta w)^3} + \frac{4T_2 \delta w}{(\tau \delta w)^2} + \frac{2}{\tau \delta w} \right)^{\frac{1}{2}} \right]^{\frac{1}{2}}$$

At zero exchange $\tau = \infty$ and δw_e , represented in this special case by δw_{∞} , is given by

$$\frac{\delta w}{\delta w_{\infty}} = \left[\frac{1}{3} - \frac{4}{3(T_2 \delta w_{\infty})^2} + \frac{2}{3} \left(1 + \frac{4}{(T_2 \delta w_{\infty})^2} + \frac{16}{(T_2 \delta w_{\infty})^4} \right)^{\frac{1}{2}} \right]^{\frac{1}{2}}$$

Using these expressions the variation of $\delta w_e / \delta w_{\infty}$ with $1/\tau \delta w$ for various values of $T_2 \delta w$ have been computed. The results are shown graphically in diagram 2.

In addition to observations on peak maxima separation⁵,

information on reaction rates have been obtained from observations on

- (i) The intensity ratio of central minimum/maximum⁹
- (ii) The band width at half height after coalescence.

Using the information briefly outlined above, equations have been derived which allows use to be made of these parameters. The resultant expressions are

$$(i) \frac{\text{Minimum intensity}}{\text{Maximum intensity}} = \frac{(1 + \tau \delta w / 2T_2 \delta w) \left[\left(\frac{P}{\delta w} \right)^2 + \frac{(S/\delta w) \left[\left(1 + \frac{\tau \delta w}{2T_2 \delta w} \right) \frac{P}{\delta w} + \frac{1}{4} \left(\frac{\delta w_e}{\delta w} \right)^2 \left(1 + \frac{\tau \delta w}{T_2 \delta w} \right)^2 \right]}{\frac{\tau \delta w}{8} \left(\frac{\delta w_e}{\delta w} \right)^2 \left(1 + \frac{\tau \delta w}{T_2 \delta w} \right)} \right]}{\left(\frac{P}{\delta w} \right)^2 + \frac{(S/\delta w) \left[\left(1 + \frac{\tau \delta w}{2T_2 \delta w} \right) \frac{P}{\delta w} + \frac{1}{4} \left(\frac{\delta w_e}{\delta w} \right)^2 \left(1 + \frac{\tau \delta w}{T_2 \delta w} \right)^2 \right]}{\frac{\tau \delta w}{8} \left(\frac{\delta w_e}{\delta w} \right)^2 \left(1 + \frac{\tau \delta w}{T_2 \delta w} \right)}}$$

$$\frac{P}{\delta w} = \frac{\tau \delta w}{2} \left[\left(\frac{1}{T_2 \delta w} \right)^2 - \frac{1}{4} \left(\frac{\delta w_e}{\delta w} \right)^2 + \frac{1}{4} \right] + \frac{1}{T_2 \delta w}$$

$$\frac{S}{\delta w} = \frac{1}{T_2 \delta w} + \frac{\tau \delta w}{2(T_2 \delta w)^2} + \frac{\tau \delta w}{8}$$

$$(ii) \frac{\delta w_1}{\delta w} = 2 \left\{ \frac{4(S/\delta w)}{\tau \delta w} \frac{\tau \delta w + T_2 \delta w}{\tau \delta w + 2T_2 \delta w} - \frac{2}{(\tau \delta w)^2} \left(1 + \frac{\tau \delta w}{T_2 \delta w} \right)^2 + 2 \left[\frac{1}{(\tau \delta w)^4} \left(1 + \frac{\tau \delta w}{T_2 \delta w} \right)^4 - \frac{4(S/\delta w)}{(\tau \delta w)^3} \frac{\tau \delta w + T_2 \delta w}{\tau \delta w + 2T_2 \delta w} \left(1 + \frac{\tau \delta w}{T_2 \delta w} \right)^2 + \frac{4(S/\delta w)^2 (\tau \delta w + T_2 \delta w)^2}{(\tau \delta w)^2 (\tau \delta w + 2T_2 \delta w)^2} + \frac{(S/\delta w)^2}{(\tau \delta w)^2} \right]^{\frac{1}{2}} \right\}^{\frac{1}{2}}$$

Both these expressions only contain terms in $T_2 \delta w$ and

DIAGRAM 3

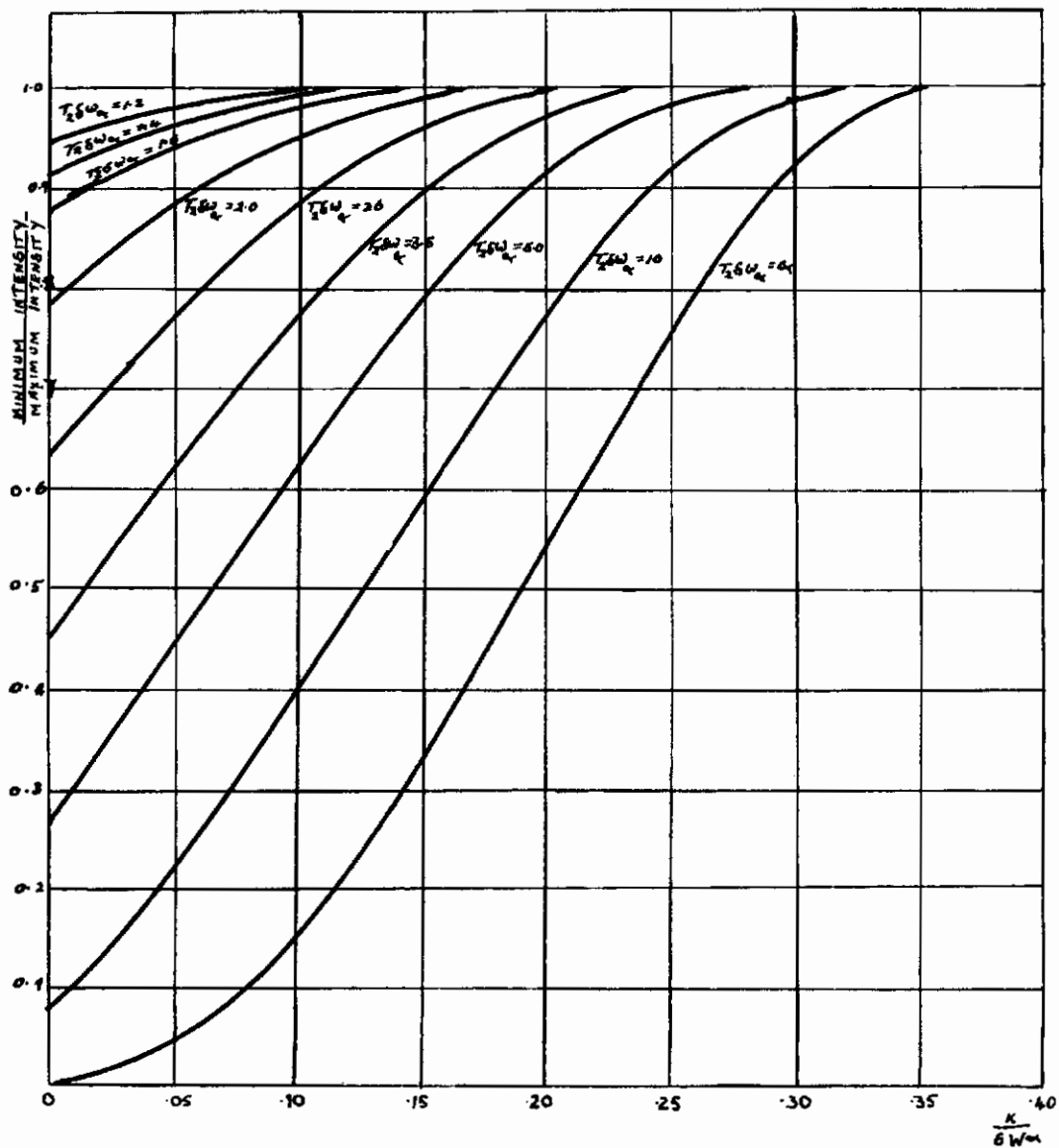
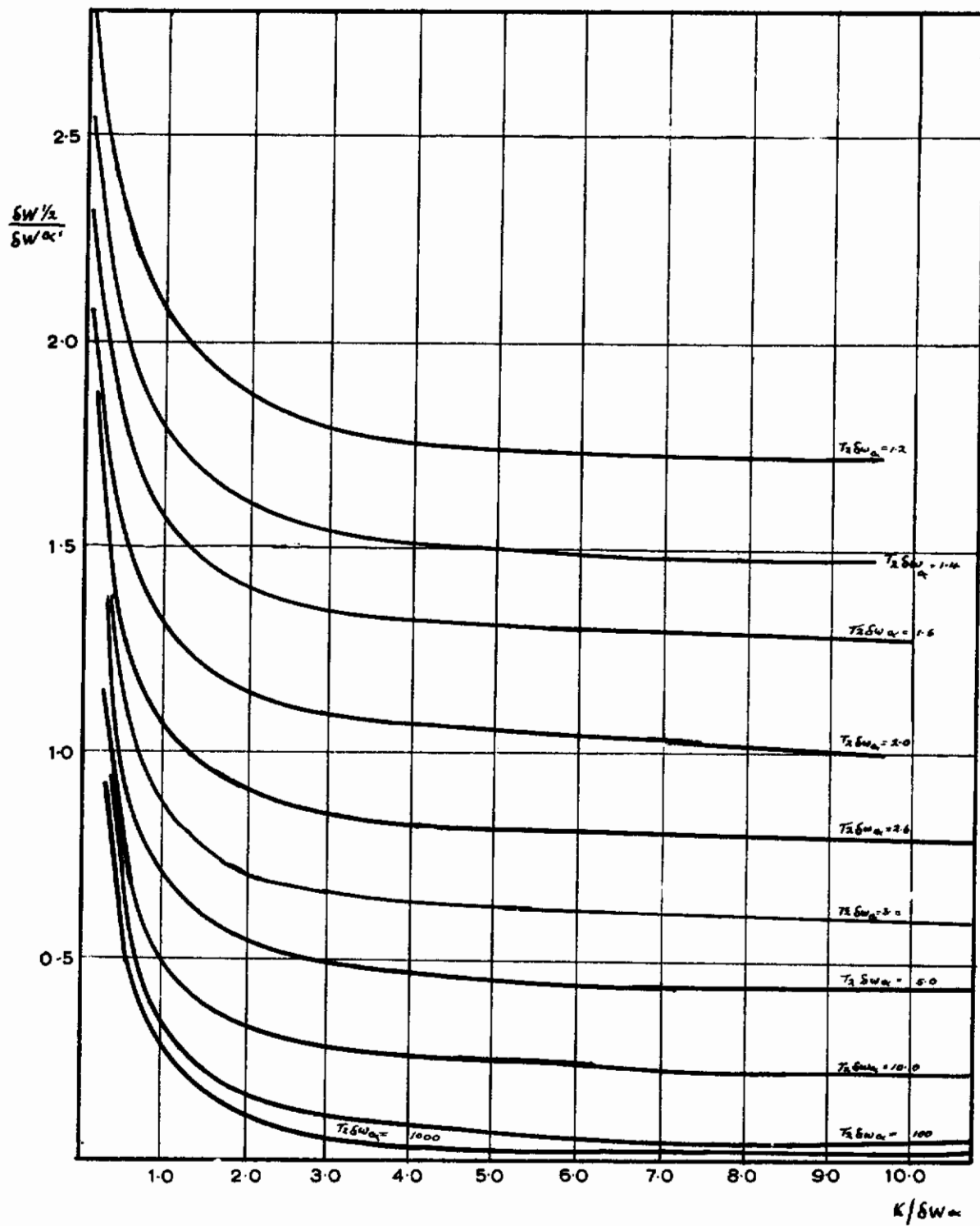


DIAGRAM 4



$1/\tau \delta w$ and therefore the variation of the appropriate parameter $\left\{ \min/\max. \text{ or } \frac{\delta w_1}{\delta w_\infty} \right\}$ with $1/\tau \delta w$ for various values of $T_2 \delta w$ can

be computed. The results of such calculations are shown in diagrams 3 and 4.

It is well known that the reaction rate constant (k) for a first order reaction = $1/\tau$.

$$\frac{1}{\tau \delta w} = \frac{k}{\delta w}$$

Observations upon (i) Separation of peak maxima
(ii) Minimum/maximum ratio
(iii) Band width at half height after coalescence will allow values of k to be calculated

from experimental observations at various temperatures. If the Arrhenius expression, $k = Ae^{-E_a/RT}$, is assumed to apply then E_a , the energy of activation for the reaction, can be calculated.

In practice the graphical results reproduced in diagrams 2, 3 and 4 are used as master graphs from which values of $k/\delta w$ can be read for each experimental observation.

| Calculated from observations on | Energy Barrier to Rotation (k.cals) based upon | | |
|--------------------------------------------------|------------------------------------------------|--------------------------------------|-------------------------------------------|
| | $T_2 \delta w_\infty = 10$ Radians | $T_2 \delta w_\infty = 5$ Radians | $T_2 \delta w_\infty = \infty$ Radians |
| Band Maxima Sep ⁿ | 14.5 | 19.4 | 5.7 |
| <u>Minimum</u> <u>Maximum</u> Intensity Ratio | 18.1 | 45.0 | 12.0 |
| Band Width at Half Height | 19.5 | 27.4 | 9.2 |
| Transition State Theory | (ΔG) = 20.7 | (ΔG) = 20.8 | (ΔG) = 20.6 |

TABLE 2. - Showing values of E_a for $C_6H_5BCl \cdot NMe_2$, at three values of $T_2 \delta w_\infty$; calculated from various experimental observations. Experimental value of $T_2 \delta w_\infty = 9.6$ Radians

A value for the energy barrier to rotation can also be calculated from the temperature at which the doublet collapses to a single peak and the value of ~~the~~ k at this temperature by substitution in the transition state expression $k = \frac{kT}{h} e^{-\Delta G^\ddagger/RT}$

Values of the energy barrier to rotation about the BN bond in phenyldimethylaminoborane, calculated from the experimental observations discussed above, are given in Table 2. Values of E_a for three values of $T_2 \delta w_\alpha$ (5, 10 and α radians) have been calculated, for each kind of experimental observation. The closest agreement occurs when $T_2 \delta w_\alpha = 10$, and this value is the nearest of the three to the value obtained experimentally (9.6 radians).

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