Journal of Organometallic Chemistry, 342 (1988) 153–157
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Organoboron compounds

XXXI *. The determination of activation parameters for the restricted rotation about the boron–nitrogen bond using ^{13}C NMR

Charles Brown, R. Harry Cragg, Tim J. Miller and David O'N. Smith

The Chemical Laboratory, University of Kent at Canterbury, Canterbury, Kent (Great Britain)

(Received September 17th, 1987)

Abstract

Variable temperature ^{13}C NMR has been used to provide reliable activation parameters $\Delta G^{\star}$, $\Delta H^{\star}$ and $\Delta S^{\star}$ for restricted rotation about the boron–nitrogen bond in a series of di-s-butylaminophenylboranes.

Introduction

For some years we have been investigating the use of ^{13}C NMR spectroscopy to examine both structure and dynamics in aminoboranes [2] and have shown that it is a reliable technique for obtaining $\Delta G^{\star}$ values for the rotational barrier about the boron–nitrogen bond in aminoboranes [3–6]. There has been considerable interest in the nature of bonding in aminoboranes owing to the π bond character of the boron–nitrogen bond, which has been compared with the isoelectronic carbon–carbon bond in olefins [7–9].

In this paper we report $\Delta G^{\star}$, $\Delta H^{\star}$ and $\Delta S^{\star}$ values for the restricted rotation about the boron–nitrogen bond in a series of substituted di-s-butylaminophenylboranes.

It is now generally accepted that the use of ^{13}C NMR has several advantages over ^{1}H NMR for the study of restricted rotation about the boron–nitrogen bond in aminoboranes.

VT ^{1}H NMR spectroscopy has a number of limitations, such as the difficulty in assignment due to overlapping peaks and time consuming determination of $\Delta H^{\star}$.

* For part XXX see Ref. 1.

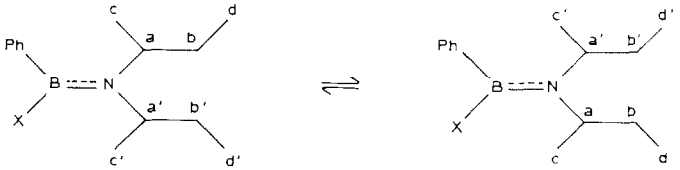
0022-328X/88/$03.50

VT ^{13}C NMR spectroscopy is a more attractive technique since the spectra are much easier to interpret, and so coalescence temperatures are more readily determined and $\Delta H^{\star}$ can be determined directly. The major limiting factor of the technique is that for an accurate determination of $\Delta H^{\star}$ the compound under investigation must have a ratio of the largest isomer shift to the smallest of at least 5 and preferably higher.

Aminoboranes such as di-n-butylaminoboranes were not suitable because the observed isomer shifts are relatively small (see Table 1). In contrast the di-s-butylaminophenylboranes were found to give ^{13}C NMR spectra with clearly resolved isomer shifts ($\Delta\nu$) for all of the carbon nuclei. In addition the isomer shifts ($\Delta\nu$) often vary by several orders of magnitude within the same molecule and exhibit a substantial range of coalescence temperatures (T_c). We have therefore been able to obtain values conveniently for $\Delta G^{\star}$ together with $\Delta H^{\star}$ and $\Delta S^{\star}$ without using the time-consuming full line-shape analysis. With a few notable exceptions [10–13] only values of $\Delta G^{\star}$ for the restricted rotation about the boron–nitrogen bond in aminoboranes have been reported.

Table 1

VT ^{13}C NMR results for substituted di-s-butylaminophenylboranes



Compound	Carbon	$\Delta\nu$ (Hz)	k_{T_c} (s^{-1})	T_c (K)	$\Delta G^{\star}$ (kJ mol^{-1})	$\Delta H^{\star}$ (kJ mol^{-1})	$\Delta S^{\star}$ (J $K\ mol^{-1}$)
Ph, F, $B{-}NBu^{s}_{2}$	a	100.1	222.2	353	70.9	76.0	12.5
	b	60.6	134.4	348	71.3		
	c	31.2	69.3	339	71.3		
	d	22.0	48.4	333	70.9		
Ph, Cl, $B{-}NBu^{s}_{2}$	a	117.0	259.9	373	74.6	65.2	26.0
	b	41.0	91.1	355	74.0		
	c	10.0	22.2	–	–		
	d	21.0	46.7	345	73.7		
Ph, Br, $B{-}NBu^{s}_{2}$	a	162.1	359.8	362	71.3	86.1	41.4
	b	69.3	153.8	349	71.1		
	c	16.0	35.5	–	–		
	d	23.9	53.1	336.5	71.5		
Ph, MeO, $B{-}NBu^{s}_{2}$	a	125.5	278.6	335	66.5	48.0	55.2
	b	68.4	151.8	322	67.6		
	c	14.2	31.4	291	62.7		
	d	24.2	54.2	306	64.7		
Ph, Cl, $B{-}NBu^{n}_{2}$ [a]	a	17.6	39.1	384	82.9		
	b	11.7	25.9	375	82.2		
	c	9.8	21.8	375	81.7		
	d	7.8	17.3	367	81.6		

[a] Ref. 4.

Results

The ^{13}C NMR spectrum of a selected aminoborane was recorded at ambient temperature and at about $-60\,^{\circ}C$ (as a 30% v/v $CDCl_3$ solution) in order to obtain values for the isomer shifts in the absence of exchange broadening. The coalescence temperature for each isomer shift was determined by recording the ^{13}C NMR spectrum at $1\,^{\circ}C$ intervals in the region of each T_c. The values for $\Delta G^{\star}$, $\Delta H^{\star}$ and $\Delta S^{\star}$ are given in Table 1.

Evaluation of $\Delta G^{\star}$

$\Delta G^{\star}$ is accessible for each isomer shift, $\Delta\nu$, and coalescence temperature, T_c, using a relationship derived by Pople [14]: $\Delta G^{\star} = 19.1\ T_c\ [9.97 + \log_{10}(T_c/\Delta\nu)]$ (kJ mol^{-1}). For isomer shifts > 50 Hz the $\Delta G^{\star}$ values should be accurate to within ± 1. kJ mol^{-1}. An error of $\pm 1\,^{\circ}C$ in T_c gives an uncertainty of 0.21 kJ mol^{-1} in $\Delta G^{\star}$ and an error of $\pm 10\%$ in $\Delta\nu$ gives an uncertainty of 0.42 kJ mol^{-1} and T_c is generally accurate to $\pm 3\,^{\circ}C$ and $\Delta\nu$ to ± 2 Hz.

Evaluation of $\Delta H^{\star}$ and $\Delta S^{\star}$

While an accurate determination of $\Delta G^{\star}$ requires knowledge of only one isomer shift and one coalescence temperature, $\Delta H^{\star}$ can only be determined when a range of at least 3 isomer shifts are known. Furthermore an accurate determination of $\Delta H^{\star}$ requires the ratio of largest isomer shift to the smallest to be at least a factor of 5.

The first order rate constant, k_{T_c}, for the rotation about the boron–nitrogen bond, can be calculated for each isomer shift, $\Delta\nu$, using a relationship which has been derived for a unimolecular process involving exchange between two equally populated species [14]: $k_{T_c} = \pi/\sqrt{2}\ \Delta\nu$ or $\sim 2.22\ \Delta\nu$. An Arrhenius plot of $\ln k_{T_c}$

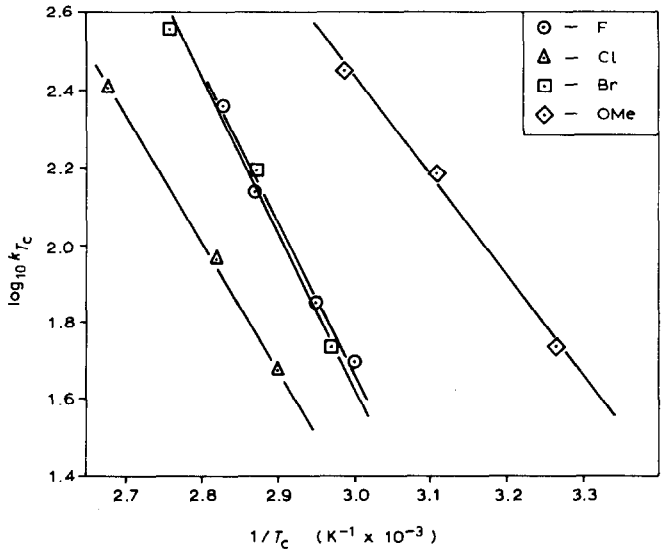


Fig. 1. Arrhenius plots for di-s-butylamino(X)phenylboranes.

against $1/T_c$ will therefore have a slope of $-\Delta H^\star/R$ from which $\Delta H^\star$ is evaluated (see Fig. 1).

$\Delta S^\star$ was evaluated using the relationship $\Delta G^\star = \Delta H^\star - T\Delta S^\star$.

Discussion

Values of $\Delta G^\star$

With a few exceptions reports on restricted solution about the boron–nitrogen bond in aminoboranes quote $\Delta G^\star$ values as an expression of the barrier to rotation. The $\Delta G^\star$ we obtained show that the halo compounds are of the same order, with an expected lower value obtained for the alkoxy compound. It is noteworthy that our value for chlorodi-s-butylaminophenylborane (74.1 kJ mol^{-1}) is the same as that determined by use of ^1H NMR [15].

Values of $\Delta H^\star$

The results indicate the following order of energy of rotation about the boron–nitrogen bond: Br > F > Cl > MeO. Except for the positions of the fluoro compound, this order is the same as that obtained for the substituted dimethylaminophenylboranes [11], and can be rationalised on electronic grounds. One might expect a greater back-donation to boron from chlorine than bromine. Such back-donation would result in a decrease in donation from nitrogen to the boron–nitrogen bond, and so a lowering of the barrier to rotation, in accord with results observed. Reports [16,17,18] suggest that oxygen is a more efficient π-donor than chlorine towards boron, and therefore the lower value observed for the methoxy compound is to be expected. The value observed for the fluoro compound needs clarification. Barfield [11] was unable to obtain a value for dimethylaminofluorophenylborane owing to the appearance of only a single methyl band in the ^1H NMR spectrum, which suggested a low barrier to rotation. We have previously demonstrated by ^{13}C NMR studies that the barrier to rotation is dialkylaminofluorophenylboranes is higher than expected [4]. In the case of dialkylaminofluorophenylboranes there are at least two factors affecting the barrier to rotation, namely (a) the high electronegativity of fluorine which would result in a high value for $\Delta H^\star$, and (b) the fact that fluorine is a more efficient π-donor towards boron than chlorine or bromine, which would reduce the barrier to rotation. The observed value of $\Delta H^\star$ for the fluoro compound suggests that the effect of (a) is greater than (b).

Values of $\Delta S^\star$

A plot of $\Delta S^\star$ vs. $\Delta H^\star$ indicates that for the halogen compounds there is an isokinetic relationship suggesting that for all these compounds a similar mechanism operates.

Experimental

The ^{13}C NMR spectra were recorded on a JEOL-PS-100 spectrometer using the FT mode and the temperature of the sample was varied by passing a stream of heated air or cold nitrogen over the probe.

The compounds used in the investigation were prepared by established methods as follows: chlorodi-s-butylaminophenylborane [19], bromodi-s-butylaminophenylborane [20], di-s-butylaminofluorophenylborane [21], di-s-butylaminomethoxyphenylborane [22] and di-s-butylaminoethanethiophenylborane [23], chloro-di-n-butylaminophenylborane [19].

References

1 Part XXX R.H. Cragg and M. Nazery, J. Organomet. Chem., 303 (1986) 329.
2 C. Brown, R.H. Cragg, T.J. Miller and D. O'N. Smith, J. Organomet. Chem., 244 (1983) 209.
3 C. Brown, R.H. Cragg, T.J. Miller and D. O'N. Smith, J. Organomet. Chem., 220 (1981) C25.
4 R.H. Cragg, T.J. Miller and D. O'N. Smith, J. Organomet. Chem., 231 (1982) C41.
5 R.H. Cragg, T.J. Miller and D. O'N. Smith, J. Organomet. Chem., 302 (1986) 19.
6 R.H. Cragg, T.J. Miller and D. O'N. Smith, J. Organomet. Chem., 291 (1985) 273.
7 H. Watanabe, K. Nagasawa, T. Totani, O. Ohashi and M. Kubo, Adv. Chem. Ser., 42 (1964) 108.
8 E. Wiberg, Naturwissensch., 35 (1948) 182.
9 M.J.S. Dewar, Adv. Chem. Ser., 42 (1964) 227.
10 C. Brown, R.H. Cragg, T.J. Miller and D. O'N. Smith, J. Organomet. Chem., 296 (1985) C17.
11 P.A. Barfield, M.F. Lappert and J. Lee, J. Chem. Soc., Trans. Farad. Soc., 64 (1968) 2571.
12 K.K. Curry and J.W. Gilje, J. Am. Chem. Soc., 98 (1976) 8262.
13 K.K. Curry and J.W. Gilje, J. Am. Chem. Soc., 100 (1978) 1442.
14 J.A. Pople, W.G. Schneider and H.J. Bernstein, High Resolution NMR, McGraw-Hill, New York, 1959.
15 D. Imbery, A. Jaeschke and H. Friebolin, Org. Mag. Res., 2 (1970) 271.
16 D.W. Aubrey, M.F. Lappert and H. Pyszora, J. Chem. Soc., (1960) 5239.
17 H.A. Skinner and N.B. Smith, J. Chem. Soc., (1954) 3930.
18 J.A. Blau, W. Gerrard, M.F. Lappert, B.A. Mountfield and H. Pyszora, J. Chem. Soc., (1960) 380.
19 R.H. Cragg and T.J. Miller, J. Organomet. Chem., 232 (1982) 201.
20 T.J. Miller, Ph.D. Thesis, University of Kent at Canterbury, 1980.
21 R.H. Cragg and T.J. Miller, J. Organomet. Chem., 217 (1981) 1.
22 R.H. Cragg and T.J. Miller, J. Organomet. Chem., 235 (1982) 135.
23 R.H. Cragg and T.J. Miller, J. Organomet. Chem., 243 (1983) 387.