Journal of Organometallic Chemistry, 244 (1983) 209–215
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

ORGANOBORON COMPOUNDS

XXII *. A ^{13}C NMR STUDY OF SOME DIALKYLAMINOPHENYLBORANES

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(Received September 17th, 1982)

Summary

The effect of substituents on the free enthalpy of rotation about the boron–nitrogen bond for the two series $PhBNMe_2X$ and $PhBNPr^i_2X$ (where X = F, Cl, Br, OMe and SEt) have been investigated by VT ^{13}C NMR.

Over the last few years we have been evaluating the use of ^{13}C NMR spectroscopy towards an understanding of the bonding in aminoboranes and also in establishing the advantages of ^{13}C NMR over ^{1}H NMR spectroscopy for obtaining information about the boron–nitrogen bond in aminoboranes [1–9]. For example, VT ^{13}C NMR spectroscopy has enabled a ΔG value for dimethylaminofluorophenylborane to be obtained [9] in contrast to previous investigations using ^{1}H NMR which were unsuccessful [13–15]. There has been considerable interest in the nature of the bonding in aminoboranes due to the π bond character of the boron–nitrogen bond which has been compared to the isoelectronic carbon–carbon bond in olefins [10–12]. A survey of the published data [13–31] obtained by ^{1}H NMR spectroscopy reveals that barriers to rotation about the boron–nitrogen bond, as expressed by $\Delta G^{\star}$, for all types of aminoboranes span a range from about 10–24 kcal mol^{-1}. In general monoaminoboranes all have relatively high rotational barriers ($\Delta G^{\star}$ 17–24 kcal mol^{-1}) while those for bisaminoboranes are usually lower ($\Delta G^{\star}$ 10–12 kcal mol^{-1}). Dewar [18] and Imbery [16] have rationalised this difference in terms of mesomeric back donation from two nitrogen atoms resulting in a mutual weakening of the boron–nitrogen π bond.

With the exception of our two notes [5,9] and a recent paper concerned with ^{13}C dynamic nuclear resonance studies of some dimesitylboryl compounds [29] there have been no reports on the application of VT ^{13}C NMR studies on aminoboranes.

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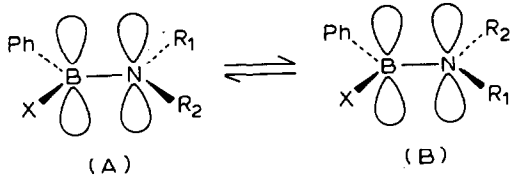
* For part XXI see Ref. 8.

0022-328X/83/0000–0000/$03.00

In this paper we report the results of our VT ^{13}C NMR studies on the aminoboranes $PhB(NMe_2)X$ and $PhB(NPr^i_2)X$ (where X = F, Cl, Br, OMe, SEt).

Results and discussion

In all the compounds studied the barrier to rotation about the boron–nitrogen bond is sufficiently high to permit the observation of separate absorption peaks from the *cis* and *trans* rotational isomers (rotomers) in the ambient temperature ^{13}C NMR spectra. For example in rotomer A below R_1 is *cis* to phenyl and 180° rotation about the boron–nitrogen bond produces rotomer B where R_1 is *trans* to phenyl and the ^{13}C NMR spectrum shows two sets of signals for the R_1 group in these two different environments.



The frequency separation between the two absorption peaks, corresponding to a particular ^{13}C nucleus in the *cis* and *trans* rotomers (the isomer shift $\Delta\nu$) depends on the difference in environment of that nucleus in the two rotomers.

The ^{13}C spectrum of a selected aminoborane was recorded at ambient temperature and at low temperature (as a 30% v/v $CDCl_3$ solution) in order to obtain all the 'no exchange isomer shifts' (i.e. the value of $\Delta\nu$, in Hz) when there is no rotation about the boron–nitrogen bond. In practice it was found that for most compounds it was only necessary to record a spectrum about 40°C below the coalescence temperature (T_c) in order to obtain the maximum value of $\Delta\nu$. The coalescence temperature for each isomer shift was determined by recording the ^{13}C NMR spectrum at 1° intervals in the region of each T_c. A value of $\Delta G^\star$ was then calculated for each isomer shift using the relationship derived by Pople [32]:

$$\Delta G^\star = 4.57\, T_c \left[9.97 + \log_{10}(T_c/\Delta\nu)\right]$$

The range of coalescence temperatures and isomer shifts observed in the case of the diisopropylaminophenylboranes was too small to warrant the calculation of activation energies. However, in view of the expected near-zero value of $\Delta S^\star$ for such intramolecular processes, the similarity of the $\Delta G^\star$ values calculated is encouraging and indicates the reliability of the results obtained.

Choice of group X in $PhB(X)NR_2$

The halogen series (F, Cl, Br) were chosen in order to investigate the mesomeric effect of the halogen on the boron–nitrogen bond. It has been well established that mesomeric back donation from a halogen to boron, in an acyclic 3-coordinate borane, increases in the sequence Br < Cl ≪ F. This sequence of increasing back donation should lower the boron–nitrogen bond order and hence $\Delta G^\star$ if it is the sole factor affecting the rotational barrier. However, the size of the halogen increases in the sequence F < Cl < Br and large groups are known to offer steric hindrance to boron–nitrogen mesomerism and thus reduce the barrier to rotation [16]. These two

effects will work in opposition to one another to produce the observed rotational barrier.

In addition methoxy- and ethylthio-groups were investigated. We have previously demonstrated that p_π–p_π back donation from oxygen to boron is more efficient than from sulphur [33] and therefore the rotational barriers for the alkylthioboranes should be higher than for the alkoxyboranes. If the results did not support this suggestion then factors other than the degree of mesomeric interaction, between the group X and boron, are important in determining the barrier to rotation.

We did not investigate bis(dialkylamino)phenylboranes as it is well established that the high degree of mesomerism from a second nitrogen atom results in a low ($\Delta G^\star \sim 10$ kcal mol^{-1}) barrier to rotation [16,18]. However ^{13}C NMR spectra of unsymmetrical bis(amino)phenylboranes indicate that in most cases there is a greater degree of back donation from one amino group than the other [4].

In addition to the dimethylamino series the diisopropylamino series was investigated in order to obtain information concerning the effect of steric hindrance on the boron–nitrogen rotational barrier.

Results

Tables 1 and 2 record the results of the VT ^{13}C NMR study on dimethylaminophenylboranes and diisopropylaminophenylboranes. It is pleasing to observe that the $\Delta G^\star$ values obtained from VT ^{1}H NMR compare very favourably with our results obtained by VT ^{13}C NMR (Table 3).

Barrier to rotation ($\Delta G^\star$)

It is evident from the results obtained and from literature reports that there are two principle factors affecting the barrier to rotation (as expressed by $\Delta G^\star$) about the boron–nitrogen bond in aminoboranes of the type PhB(NR_2)X namely:

(a) the steric effect of NR_2;

(b) the combined steric, mesomeric and inductive effects of X.

These effects collectively produce the observed barrier to rotation and may well work in opposition to one another. Thus compounds in Tables 1 and 2 were carefully chosen so that each effect could be studied independently.

(a) The steric nature of the NR_2 group. Our results reveal that $\Delta G^\star$ values for each

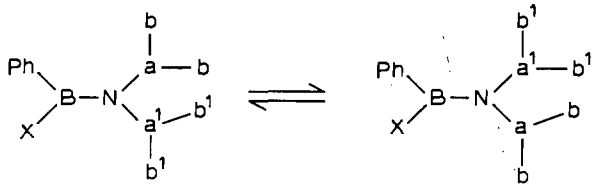
TABLE 1

VT ^{13}C NMR RESULTS FOR DIMETHYLAMINO(X)PHENYLBORANES

Compound	$\Delta\nu$ Hz	KT_c (s^{-1})	T_c (K)	$\Delta G^\star$ (kcal mol^{-1})
Ph, F > B–NMe_2	54.2	120.3	386	19.1
Ph, Cl > B–NMe_2	14.6	32.4	373	19.4
Ph, Br > B–NMe_2	41.0	91.0	402.5	20.1
Ph, MeO > B–NMe_2	84.0	186.5	329	15.9
Ph, EtS > B–NMe_2	44.0	97.7	378	18.8

TABLE 2

VT ^{13}C NMR RESULTS FOR DIISOPROPYLAMINO(X)PHENYLBORANES



Compound	Carbon	$\Delta\nu$ (Hz)	KT_c (s^{-1})	T_c (K)	ΔG^* (kcal mol^{-1})
Ph, F >B–NPr^i_2	a	109.9	243.9	351	16.8
	b	54.9	121.9	340	16.7
Ph, Cl >B–NPr^i_2	a	149.4	331.7	359	17.0
	b	36.1	80.1	340	17.0
Ph, Br >B–NPr^i_2	a	166.0	368.5	350	16.5
	b	38.1	84.6	330	16.5
Ph, MeO >B–NPr^i_2	a	127.0	281.9	307.5	14.5
	b	43.0	95.5	291	14.4
Ph, EtS >B–NPr^i_2	a	91.6	203.4	253	17.0
	b	6.7	14.9	315	16.8

member of the $PhB(NPr^i_2)X$ series are some 2–3 kcal mol^{-1} lower than the corresponding members of the $PhB(NMe_2)X$ series. The value of ΔG^* falls markedly as the amino group becomes more bulky and this can be rationalised in terms of effect of steric hindrance to mesomerism. For the two series the effect is best

TABLE 3

A COMPARISON OF ΔG^* VALUES WITH LITERATURE VALUES

Compound	VT ^{13}C NMR		VT ^1H NMR	
	ΔG^* (kcal mol^{-1})	Ref.	ΔG^* (kcal mol^{-1})	Ref.
$PhB(NMe_2)Cl$	19.4		20.1	[15]
			18.9	[15]
			19.8	[15]
			20.3	[16]
			20.6	[31]
$PhB(NMe_2)Br$	20.2		19.8	[15]
			20.7	[15]
			20.2	[15]
$PhB(NMe_2)OMe$	15.9		14.0	[15]
			21.6	[15]
			15.5	[15]
$PhB(NPr^n_2)Cl$	19.6	[5]	19.2	[16]
$PhB(NPr^i_2)Cl$	17.0		17.0	[16]
$PhB(NBu^n_2)Cl$	19.7	[5]	19.7	[16]

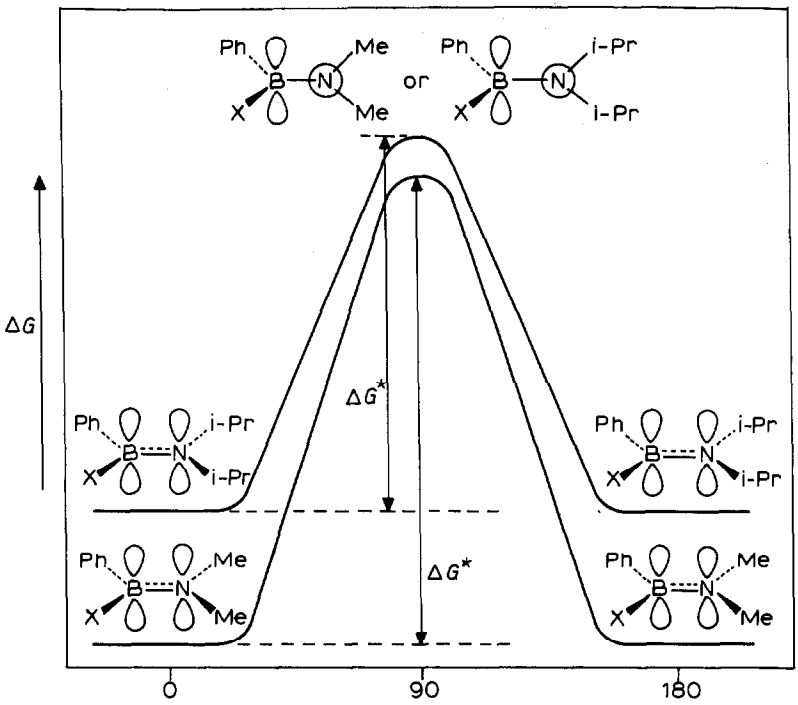


Fig. 1. ΔG versus angle of rotation about the B–N bond.

rationalised by constructing an energy diagram of $\Delta G^{\star}$ versus the angle of rotation about the boron–nitrogen bond (Fig. 1). The ground state (or minimum energy conformation) is taken to be a flat molecule (i.e. the PhBX and NR_2 units are coplanar) with maximum p_{π}–p_{π} overlap. The transition state is achieved by 90° rotation about the boron–nitrogen bond and in this position the boron and nitrogen p orbitals are orthogonal i.e. no p_{π}–p_{π} stabilising interaction. The ground states for diisopropylamino(X)phenylboranes will be higher in free energy (i.e. less stable) than those for the dimethylamino(X)phenylboranes because the greater steric hindrance of the diisopropylamino group makes it more difficult to achieve a coplanar molecule. Thus by raising the free energy of the ground state $\Delta G^{\star}$ is reduced. The relatively high barrier to rotation for chloro-di-n-butylaminophenylborane ($\Delta G^{\star}$ 19.7 kcal mol^{-1}) [5] further illustrates that it is not necessarily the length of the alkyl chain in the dialkylamines group which lowers $\Delta G^{\star}$ but the steric effects resulting from branching i.e. from the bulk of the alkyl group.

(b) The combined steric, inductive and mesomeric effects of X. Examining $\Delta G^{\star}$ values in Tables 1 and 2 the following generalisation can be made. When the amino group is unhindered (e.g. NMe_2) the electronic effect of X governs the barrier to rotation, but when the amino group is very hindered (e.g. $N(Pri)_2$) the steric effect of X becomes more important. In the dimethylamino series $\Delta G^{\star}$ values increase in the sequence F < Cl < Br which is in accord with electronic expectations. However in the diisopropylamino series the fluoro compound actually has a higher barrier to rotation than the bromo compound, reflecting the smaller size of fluorine which offers less steric hindrance to B–N mesomerism than bromine when the amino group is bulky.

It is observed that methoxy compounds have $\Delta G^{\star}$ values around 15 kcal mol^{-1}, while the corresponding ethylthio compounds have $\Delta G^{\star}$ values some 3–4 kcal mol^{-1} higher, which are on a par with the halogen compounds. This indicates the greater p_{π}–p_{π} back donation from oxygen to boron, compared to sulphur, which is due to the better match of oxygen and boron p orbitals.

The following generalisation can be made concerning the mesomeric effect of X in compounds of the type $PhBNR_2X$, where NR_2 is unhindered: X groups such as halogens, organyls and SR, which give little back donation, have $\Delta G^{\star}$ values approaching 20 kcal mol^{-1}; methoxy groups, giving greater back donation, have $\Delta G^{\star}$ values of about 15 kcal mol^{-1}; while bisamino compounds, where there is back donation from 2 nitrogen atoms have $\Delta G^{\star}$ values of only about 10 kcal mol^{-1}. This generalisation is only valid when X is also unhindered.

Conclusions

The following conclusions can be made about restricted rotation (about the B–N bond) in aminoboranes of the type $PhBNR_2X$ and the application of VT ^{13}C NMR to the study of the barrier to rotation in these systems.

(a) When NR_2 is small the barrier to rotation is governed principally by the mesomeric and inductive effect of X.

(b) When NR_2 is bulky the steric effect of X affects the rotational barrier to a larger extent.

(c) As the steric hindrance of NR_2 is increased (e.g. from $NMe_2 \rightarrow N(Pri)_2$) the rotational barrier falls.

(d) The rotational barrier results principally from p_{π}–p_{π} back donation from nitrogen to boron, but when the amino groups are excessively bulky then there is also an inherent steric resistance to rotation which contributes to restricted rotation.

(e) VT ^{13}C NMR is an excellent method for evaluating accurately the barrier to rotation as expressed by $\Delta G^{\star}$.

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. An error of ± 1 K in T_c gives an uncertainty of 0.05 kcal mol^{-1} in $\Delta G^{\star}$ and an error of $\pm 10\%$ in $\Delta \sim$ an uncertainty of 0.01 kcal mol^{-1} in $\Delta G^{\star}$. Since T_c is generally accurate to ± 3 K and $\Delta\nu$ to ± 2 Hz the calculated $\Delta G^{\star}$ values reported are accurate to within ± 0.25 kcal mol^{-1}.

The compounds used in the investigation were prepared by established methods namely dialkylaminofluorophenylboranes [2,14] chlorodialkylaminophenylboranes [6,14], bromodialkylaminophenylboranes [14,34], dialkylaminomethoxyphenylboranes [7,14] and dialkylaminoethylthiophenylboranes [34].

Acknowledgement

We thank the S.R.C. for financial support.

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