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ORGANOBORON COMPOUNDS

XXVII *. A ^{13}C NMR STUDY OF $PhB(NMe_2)NHBu^t$ AND $PhB(NMe_2)NHSiMe_3$

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Summary

The rotational barriers ($\Delta G^\star$) about the $>B{-}NMe_2$ bond in $PhB(NMe_2)NHBu^t$ and $PhB(NMe_2)NHSiMe_3$ have been determined by variable temperature ^{13}C NMR.

Introduction

For some time we have been investigating the application of ^{13}C NMR towards an understanding of the factors affecting the nature of the $p\pi{-}p\pi$ bonding in aminoboranes [1]. Until our more recent studies the most commonly used method of estimating the boron–nitrogen rotational barrier in aminoboranes, as expressed by $\Delta G^\star$, has involved use of variable temperature ^1H NMR. The use of variable temperature ^{13}C NMR in estimating the boron–nitrogen rotational barrier in aminoboranes is attractive since the spectra are more easily interpretated than the corresponding ^1H NMR spectra and as a result coalesence temperatures are more easily determined.

Results and discussion

The ^{13}C NMR spectra of the title compounds at low temperature show methyl non equivalence with the peaks coalescing at $-25°C$ for butylaminodimethylaminophenylborane (**A**) and 8°C for dimethylaminophenyltrimethylsilylaminoborane (**B**).

Using the relationship, $\Delta G^\star = 4.57\ Tc\ [9.97 + \log_{10}(\frac{Tc}{\Delta\nu})]$, derived by Pople [2], values of $\Delta G^\star$ for **A** and **B** were obtained from each pair of resonances arising from

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* For part XXVI see ref. 5.

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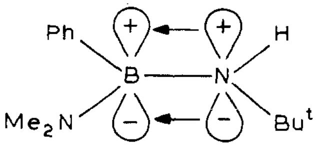


Fig. 1

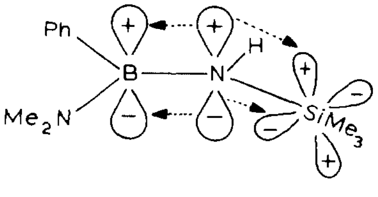


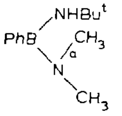
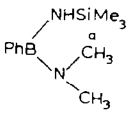
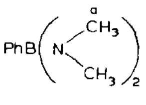
fig. 2

isomer shifts $\Delta\nu$ and coalescence temperature Tc. The $\Delta G^\star$ value for **A**, the first reported value for an aminodialkylaminophenylborane, is higher than values obtained for bisdialkylaminophenylborane, using variable temperature ^{1}H NMR and, surprisingly, the $\Delta G^\star$ value obtained for **B** is even higher. This result indicates that $p\pi$–$p\pi$ bonding between boron and the t-butylamino group is greater than that between boron and the trimethylsilylamino group.

In comparing the $\Delta G^\star$ results for compounds **A** and **B** it is attractive to suggest that the higher $\Delta G^\star$ value exhibited by compound **B** is due to the $p\pi$–$d\pi$ bonding

TABLE 1

SOME ^{13}C NMR AND $\Delta G^\star$ DATA FOR COMPOUNDS A, **B** AND PhB(NMe$_2$)$_2$

Compound	Carbon	$\Delta\nu$ (Hz)	Tc	$\Delta G^\star$(kcal mol^{-1})
 (**A**)	a	82.4	−25	11.86
 (**B**)	a	92	8	13.5
	a	33	−60	10.5 [3,4]

between nitrogen and silicon, as shown in Fig. 2, which reduced the $p\pi$–$p\pi$ bonding between boron and the nitrogen of the trimethylsilyamino group. This of course cannot occur in compound **A** (Fig. 1.)

The result of a weakening of the $p\pi$–$p\pi$ bonding between the boron and nitrogen of the trimethylsilylamino or t-butylamino groups in these compounds would have the effect of increasing the $p\pi$–$p\pi$ bonding between boron and nitrogen of the dimethylamino group, and this would account for the observed $\Delta G^{\star}$ values.

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. Some results are listed in Table 1. An error of ± 1 K in Tc gives an uncertainty of 0.05 kcal mol^{-1} in $\Delta G^{\star}$ and an error of $\pm 10\%$ in Δ an uncertainty of 0.01 kcal mol^{-1} in $\Delta G^{\star}$. Since Tc is generally accurate to ± 3 K and $\Delta\nu$ to ± 2Hz 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 [6].

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