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Preliminary communication

RESTRICTED ROTATION ABOUT THE B—N BOND IN AMINOBORANES: THE DETERMINATION OF ACTIVATION PARAMETERS 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)

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Summary

In suitable cases, VT ^{13}C NMR can provide a rapid and reliable method for obtaining activation parameters $\Delta H^\star$ and $\Delta S^\star$ for restricted rotation about the B — N bond in aminoboranes.

Over the past few years we have been using ^{13}C NMR to examine structure and dynamics in aminoboranes [1—3]. In particular, VT ^{13}C NMR has proved itself especially useful in the study of isomerism arising from restricted rotation about the boron—nitrogen bond. Typically ^{13}C NMR spectra of aminoboranes show clearly resolved isomer shifts ($\Delta\nu$) for many or all of the carbon nuclei, unlike the ^{1}H spectra which usually suffer from smaller isomer shifts and troublesome overlap of signals. A particularly valuable feature of these isomer shifts is that they often vary within the same molecule by factors approaching two powers of ten, and exhibit a correspondingly substantial range of coalescence temperatures (T_c). This provides the basis for a convenient and reliable method of obtaining $\Delta H^\star$ and $\Delta S^\star$ parameters without recourse to time-consuming full line-shape analysis, and we demonstrate the method in the present article. This should add considerably to our understanding of the process of B—N bond rotation, as with notable exceptions [4,5], only $\Delta G^\star$ data for aminoboranes appear in the literature [3].

Raban [6] has shown that the rate constant for coalescence can be reliably determined for coalescing singlets from the simple equation 1.

$$k_c = \frac{\pi \Delta \nu}{v^2} \tag{1}$$

Therefore by measuring the coalescence temperature for each isomer shifted pair, and calculating the rate constant at each temperature we can construct

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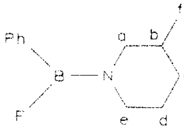
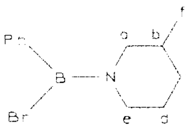
TABLE 1

VT ^{13}C NMR DATA FOR FLUORO-3-METHYLPIPERIDINOPHENYLBORANE AND BROMO-3-METHYLPIPERIDINOPHENYLBORANE

Compound	Carbon	$\Delta\nu$ (Hz)	kT_c (s^{-1})	T_c (K)	$\Delta G^\star$ (kcal mol^{-1})	$\Delta H^\star$ (kcal mol^{-1})	$\Delta S^\star$ (kcal mol^{-1})
	a	56.9	126.3	388	19.2	19.0	−1.1
	b	12.2	27.1	371	19.4		
	c	2.9	6.5	346	19.0		
	d	6.8	15.2	356	19.0		
	e	56.9	126.3	388	19.2		
	f	3.0	6.7	—	—		
	a	26.4	58.5	390	19.9	16.5	−7.6
	b	18.6	41.2	385	19.9		
	c	1.7	3.8	341	19.1		
	d	16.6	36.9	382.5	19.8		
	e	28.3	62.9	392	20.0		
	f	3.9	8.7	359	19.6		

a satisfactory Arrhenius plot from which $\Delta H^\star$ and $\Delta S^\star$ can be obtained. The ^{13}C NMR spectra of fluoro-3-methylpiperidinophenylborane and bromo-3-methylpiperidinophenylborane were recorded over a range of temperatures in order to determine the isomer shifts in the absence of exchange broadening, and the coalescence temperature of each isomer shifted line pair (Table 1). From these we calculated the $\Delta H^\star$ and $\Delta S^\star$ values as described above.

A value of $\Delta G^\star$ can be obtained from each pair of resonances arising from isomer shifts, $\Delta\nu$, and coalescence temperature, T_c, using the relationship $\Delta G^\star = 4.57\ T_c\ (9.97+\log_{10}(T_c/\Delta\nu))$. An error of ± 1°C in T_c gives an uncertainty of 0.05 kcal mol^{-1} in $\Delta G^\star$ and an error of ± 10% in $\Delta\nu$ gives an uncertainty of 0.1 kcal mol^{-1} in $\Delta G^\star$. Since T_c is generally accurate to ± 3 K and $\Delta\nu$ to ± 2 Hz then $\Delta G^\star$ values should be accurate to within ± 0.25 kcal mol^{-1}.

The results obtained demonstrate the value of VT ^{13}C NMR in the determination of extra-thermodynamic parameters for aminoboranes.

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