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Preliminary communication

RESTRICTED ROTATION ABOUT THE BORON—NITROGEN BOND IN AMINOBORANES

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Summary

The application of variable temperature ^{13}C NMR to the study of a series of chlorodialkylaminophenylboranes has enabled $\Delta G^\star$ values for the rotational barrier, about the boron—nitrogen bond, to be determined.

For many years there has been considerable interest in the factors influencing p_π—p_π bonding in aminoboranes. One technique which has had considerable success is that of variable temperature ^1H NMR [1—7]. However this technique has a number of limitations, in particular the difficulty of assignments due to overlapping peaks. We have recently begun a reinvestigation of the problem using VT ^{13}C NMR. This technique is attractive in so far as the spectra are more easily interpreted than the corresponding ^1H NMR spectra and as a result coalescence temperatures are more easily determined.

We have studied a series of chlorodialkylaminophenylboranes by VT ^{13}C NMR and the value of the technique can be seen from the results in the table. A value of $\Delta G^\star$ was obtained from each pair of resonances arising from isomer shifts, $\Delta\nu$, and coalescence temperature, T_c, using the relationship $\Delta G^\star = 4.57\ T_c[9.97 + \log_{10}(T_c/\Delta\nu)]$ derived by Pople [8]. The range of coalescence temperatures observed for any one compound was too small to warrant 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 for those compounds exhibiting more than one coalescence temperature is encouraging and indicates the reliability of the results obtained.

We are at present extending our studies to evaluate the potential application of ^{13}C NMR to study the factors which influence restricted rotation about boron—nitrogen bonds in aminoboranes.

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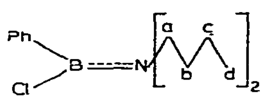
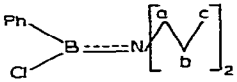
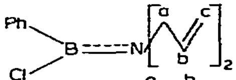
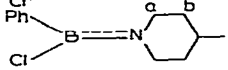
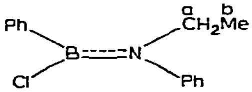
TABLE 1

VT ^{13}C NMR RESULTS FOR CHLORO(DIALKYLAMINO)PHENYLBORANES

Compound	Carbon	$\Delta\nu$	kT_c	T_c	$\Delta G^{\star}$ [b]
 [a]	a	17.6	39.1	384	19.8
	b	11.7	25.9	375	19.7
	c	9.8	21.8	375	19.8
	d	7.8	17.3	367	19.5
	a	19.6	43.5	383	19.7
	b	9.8	21.8	371	19.6
	c	9.8	21.8	371	19.6
	b	19.5	43.3	369	19.0
	a	9.8	21.8	366	19.3
	a	20.5	45.5	350	17.9
	b	15.6	34.6	339.5	17.5
	a	106.8	237.1	383	18.4

[a] Note a $\Delta G^{\star}$ value of 19.7 kcal/mol, obtained by ^{1}H NMR, has been reported for PhB(NBu$^{n}_{2}$)Cl [6].
[b] Accurate to within ± 0.25 kcal/mol.

References

1 P.A. Barfield, M.F. Lappert and J. Lee, Proc. Chem. Soc., (1961) 421.
2 G.E. Ryschkewitsch, W.S. Brey and A. Saji, J. Am. Chem. Soc., 83 (1961), 1010.
3 H. Baechle, H.J. Becher, H. Beyer, W.S. Brey, J.W. Dawson, M.E. Fuller and K. Niedenzu, Inorg. Chem., 2 (1963) 1065.
4 P.A. Barfield, M.F. Lappert and J. Lee, J. Chem. Soc., (1968) 554.
5 K.N. Scott and W.S. Brey, Inorg. Chem., 8 (1969) 1703.
6 D. Imbery, A. Jaeschke and H. Friebolin, Org. Mag. Res., 2 (1970) 271.
7 P.A. Barfield, M.F. Lappert and J. Lee, Trans. Farad. Sco., (1968) 2571.
8 J.A. Pople, W.G. Schneider and H.J. Bernstein, High Resolution NMR, McGraw Hill, New York, 1959.