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ORGANOBORON COMPOUNDS

XXIX *. A COMPARISON OF p_π–p_π BONDING IN ALKOXY AND ALKYLTHIOPIPERIDINOPHENYLBORANES

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Summary

The results of a VT ^{13}C NMR study of alkoxy and alkylthio derivatives of 2- and 3-methylpiperidinophenylboranes demonstrate that the p_π–p_π bonding between boron and oxygen is some 3 kcal mol^{-1} stronger than that between sulphur and boron.

We have for some time been investigating the nature of p_π–p_π bonding in organoboranes. The results of our proton magnetic resonance studies concerning the interaction between trialkylthioboranes and trialkoxyboranes with pyridine and γ-picoline strongly suggested that p_π–p_π bonding between boron and oxygen is greater than between boron and sulphur [2]. However, it has been suggested that for planar boron compounds boron–oxygen and boron–sulphur p_π–p_π bonding are of similar magnitudes [3].

In this paper we report our results of a VT ^{13}C NMR study of alkoxy and alkylthio derivatives of 2- and 3-methylpiperidinophenylboranes. The compounds for investigation were carefully chosen with two objectives in mind, namely (i) to compare the effect on the ΔG^* values for the p_π–p_π bonding of alkoxy and alkylthiomethylpiperidinophenylboranes, and (ii) to determine the effect of steric hindrance.

Although there have been many studies of the restricted rotation about the boron–nitrogen bond in aminoboranes [4–6], reports on aminoboranes in which one of the substituents is an alkoxy or an alkylthio group are very limited [4,7]. In addition except for our own work [8–10], all the reported ΔG^* values for the restricted rotation about the boron–nitrogen bond have come from ^1H NMR studies. We have previously demonstrated the value of ^{13}C NMR in obtaining information on the rotational barrier about the boron–nitrogen bond in

* For part XXVIII see ref. 1.

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aminoboranes, and it will be appreciated that the ^{1}H NMR spectra of the compounds discussed in the present paper are too complex for any meaningful information to be obtained.

Results and discussion

In the compounds investigated the barrier to rotation about the boron–nitrogen bond is sufficiently high to allow the observation of separate peaks from the *cis* and *trans* rotational isomers in the ^{13}C NMR spectra at ambient temperature. Tables 1 and 2 record the results of the VT ^{13}C study on the titled compounds. The values of $\Delta G^{\star}$ were obtained from each pair of resonances arising from isomer shifts, $\Delta\nu$, and coalescence temperature T_c, using the relationship $\Delta G^{\star} = 4.57\, T_c[9.97 + \log_{10} T_c/\Delta\nu]$. The results obtained suggest at least two major factors which affect the barrier to rotation namely: (a) steric effects, and (b) combined steric, mesomeric and inductive effects of the alkoxy and alkylthio groups.

(a) Steric effects

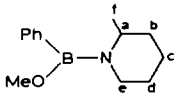
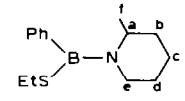
For maximum p_π–p_π bonding between boron and nitrogen the molecule has to be planar, and this is more easily achieved in the 3-methylpiperidino rather than the 2-methylpiperidino systems. Thus one would expect, and our results show, that $\Delta G^{\star}$ values for the 2-methylpiperidino derivatives are lower (by some 2 kcal mol^{-1}) than those for the corresponding 3-methylpiperidino derivatives. These observations support previous reports on the effect of an increase in steric hindrance in amines on the restricted rotation about the boron–nitrogen bond [7].

(b) Combined steric, mesomeric and inductive effects

The results indicate that the barrier to rotation in the alkoxy compounds is about 3 kcal mol^{-1} lower than that for the alkylthio compounds. It is noteworthy that a similar result was observed for the alkoxy and alkylthio derivatives of dimethyl-

TABLE 1

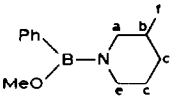
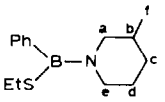
VT ^{13}C NMR RESULTS FOR 2-METHYLPIPERIDINOPHENYLBORANES [a]

Compound	δ(C) (ppm)	$\Delta\nu$ (Hz)	kT_c (s^{-1})	T_c (K)	$\Delta G^{\star}$ (kcal mol^{-1})
	a	91.8	203.8	290	13.9
	b	12.7	28.2	NM	–
	c	0	0	–	–
	d	14.6	32.4	NM	–
	e	94.7	210.2	290	13.9
	f	6.8	15.1	NM	–
	a	29.5	65.5	342	17.3
	b	16.6	36.9	335	17.5
	c	0	0	–	–
	d	14.6	32.4	333	17.3
	e	37.1	82.4	349	17.2
	f	0	0	–	–

[a] NM = not measured.

TABLE 2

VT ^{13}C NMR RESULTS FOR 3-METHYLPIPERIDINOPHENYLBORANES [a]

Compound	δ(C) (ppm)	Δν (Hz)	kT_c (s^{-1})	T_c (K)	ΔG^* (kcal mol^{-1})
	a	86.9	192.9	333	16.1
	b	12.7	28.2	307.5	16.0
	c	0	–	–	–
	d	19.5	43.3	312	15.9
	e	87.9	195.1	333	16.1
	f	8.8	19.5	NM	–
	a	33.6	74.6	383	19.3
	b	12.2	27.1	NM	NM
	c	0	0	–	–
	d	24.4	54.2	NM	NM
	e	33.6	74.6	383	19.3
	f	6.1	13.5	NM	NM

[a] NM = not measured.

aminophenylborane and di-i-propylaminophenylborane [7].

The electronegativity of oxygen is greater than sulphur, and therefore we would expect a higher barrier to rotation in the alkoxy than in the alkylthio derivatives. The results indicate however, that the mesomeric effects are predominant, and that the p_π–p_π bonding between boron and oxygen is stronger than that between boron and sulphur.

Experimental

The ^{13}C NMR spectra were recorded on a JEOL-PS-100 spectrometer using the FT mode. An error of ±1 K in T_c gives an uncertainty of 0.05 kcal mol^{-1} in ΔG^* and an error of ±10% in Δν an uncertainty of 0.1 kcal mol^{-1} in ΔG^*. Since T_c is generally accurate to ±3 K and Δν to ±2 Hz, the calculated ΔG^* values reported are accurate to within ±0.25 kcal mol^{-1}.

The compounds used in the investigation were prepared by established methods as follows: methoxy-2-methylpiperidinophenylborane [11], methoxy-3-methylpiperidinophenylborane [11], ethanethio-2-methylpiperidinophenylborane [12], and ethanethio-3-methylpiperidenophenylborane [12].

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