

CONTRIBUTIONS TO ORGANOBORON CHEMISTRY

XV *. AMINODIPHENYLBORANES

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Summary

The synthesis of a series of aminodiphenylboranes is reported together with the results of a detailed study of their ^{13}C NMR spectra. All compounds exhibited peaks assignable to the carbon atom directly bonded to boron when run under appropriate conditions. The ^{13}C spectra of primary aminodiphenylboranes provided further evidence for restricted rotation about the B–N bond.

For many years there has been considerable interest concerning $p_{\pi}-p_{\pi}$ interactions between boron and nitrogen in aminoboranes [1]. However, much evidence has been based upon ^1H NMR spectra [2]. By contrast, although ^{13}C NMR has advantages over ^1H NMR, there have been until recently few reports concerning the ^{13}C NMR spectra of phenylorganoboranes [3–9]. The application of ^{13}C NMR to the study of organoboranes ** has to some extent been hindered by effects due to quadrupolar nature of the boron nucleus (^{11}B , $I = 3/2$; natural abundance 82%) in that resonances arising from carbon directly attached to boron (C(1) carbons) are not easily detected. Thus several groups have reported difficulties in observing C(1) resonances [5,9–12]; the signal being very broadened or entirely undetectable. Until recently the only methods available for obtaining C(1) chemical shifts were time consuming low temperature measurements [5] or heteronuclear triple resonance experiments [9]. The only compounds which yielded C(1) directly were those with zero electric field gradient at boron and these are effectively limited to boron anions where all four ligands are identical, e.g. $\text{Na}^+\text{BPh}_4^-$ [13]. However, we recently reported

* For part XIV see ref. 22.

** During the preparation of this paper we became aware of the recent publication concerning aminodimesitylboranes (8).

[3] that in the majority of cases the $C(1)$ values can be obtained conveniently by recording the spectra of neat samples. We are at present evaluating the application of ^{13}C NMR studies to organoboranes and in the present paper we report our results on aminodiphenylboranes. Our interest in this class of compounds was to demonstrate the value of the technique compared to ^1H NMR in obtaining information about $p_\pi-p_\pi$ bonding in aminoboranes and also to attempt to evaluate factors affecting the nature of $p_\pi-p_\pi$ bonding.

Alkylaminodiphenylboranes (Ph_2BNHR)

These compounds were obtained as mobile liquids from the interaction of chlorodiphenylborane and the corresponding amine. The monomeric nature of the compounds was demonstrated by the position in the infrared spectrum of the $\nu(\text{N-H})$ frequency. In these compounds $p_\pi-p_\pi$ bonding results in partial double bond character across the B-N bond, giving rise to restricted rotation about the B-N bond. However, because two of the groups bonded to boron are identical, isomer shifts are not observed in the NMR spectra for lines associated with the amino group. In contrast the phenyl groups show isomer shifts, with separate signals resulting from the phenyl group *cis* and the phenyl group *trans* to R.

^1H NMR spectra

As expected, in all cases only one set of resonances for the primary amino

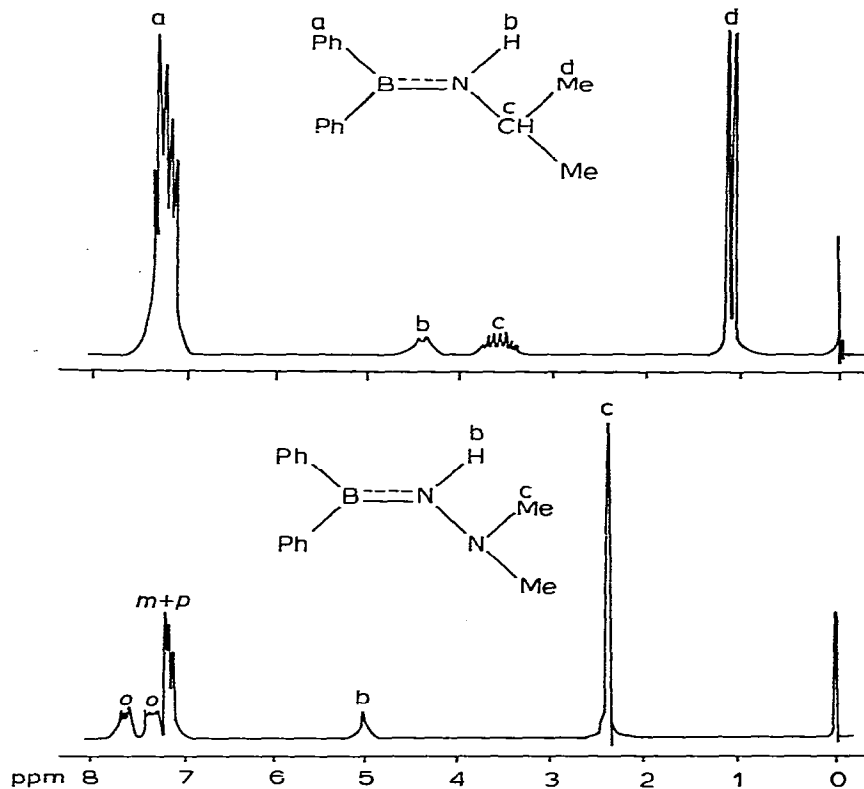


Fig. 1. A comparison of the ^1H NMR spectra of $\text{Ph}_2\text{BNHNMe}_2$ and PhBNHCHMe_2 .

group was detected. The signals for the phenyl groups consisted of a broad single band and hence no valuable information could be obtained. Figure 1 shows a typical example of the ^1H NMR spectrum of an aminodiphenylborane. However in the case of N,N' -dimethylhydrazinodiphenylborane the aromatic resonances were split into three separated bands in the ratio of 1 : 1 : 3 with the two smaller bands tentatively assigned to the *ortho* hydrogens of each rotamer. It is instructive to compare this spectrum with that of the isoelectronic and isostructural compound 1-propylaminodiphenylborane (Fig. 1) since the spectrum of the latter is typical, in the aromatic region, of the other seven compounds investigated.

The results indicate that the hydrazino group gives much larger isomer shifts. This behaviour was also observed in the ^{13}C NMR spectra, recorded at ambient temperature, and may be attributed to the greater anisotropy of the N—N bond.

^{13}C - $\{^1\text{H}\}$ spectra

In contrast to the ^1H NMR spectra it was found that where broad envelopes were observed for aromatic proton resonances, sharp lines were observed for aromatic carbons. The *ortho* carbon resonances appeared as equally intense pairs in all compounds studied and in most cases the *meta* carbon resonances were also split. In addition in a few cases, where the spectra were recorded on neat samples, the C(1) resonances were also split. However in all cases the *para* carbon resonances were single sharp lines as were the resonances associated with the alkyl amino groups. The spectrum of *t*-butylaminodiphenylborane (Figure 2) is typical. The resonances assigned to C(1), *o*- and *m*-carbon atoms are observed as equally intense pairs which on warming to 180°C coalesce to singlets. This high barrier to rotation, though principally electronic, probably has some steric component.

In view of the differences in the ^1H NMR spectra of the isoelectronic $\text{Ph}_2\text{BNHNMe}_2$ and $\text{Ph}_2\text{BNHCHMe}_2$, it is instructive to compare their ^{13}C NMR spectra (Figure 3). The spectra reveal much larger isomer shifts for the hydrazino compound. Indeed the separation of 67 Hz observed for the *ortho* carbon resonance is the largest of all compounds studied. The magnitude of the isomer

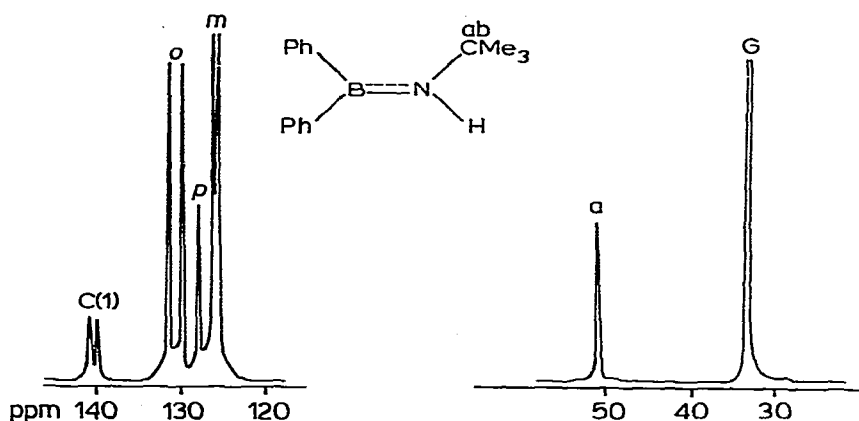


Fig. 2. The ^{13}C NMR spectrum of $\text{Ph}_2\text{BNHt-Bu}$.

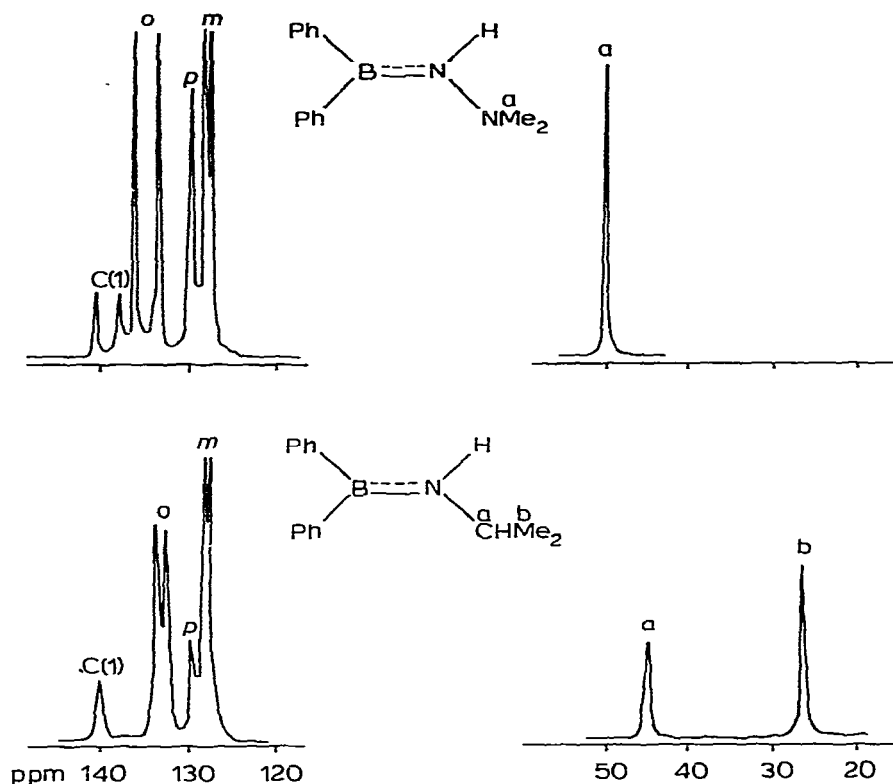
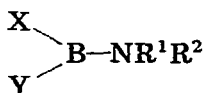


Fig. 3. The contrasting ^{13}C NMR spectra of $\text{Ph}_2\text{BNHNMe}_2$ and Ph_2BNHiPr .

shift is not in itself a measure of the barrier to rotation about the B–N bond or the degree of B–N p_π – p_π bonding but a measure of the difference in shielding between the phenyl group *cis* to the hydrazino group and the phenyl group *trans* to the hydrazino group. The large isomer shift could be accounted for by the extra nitrogen atom of the hydrazino group producing greater differential shielding than a normal alkyl group.

Table 1 lists the assignments of the ^{13}C spectra of the aminodiphenylboranes studied. No attempt has been made to determine which resonance in each 1 : 1 pair belongs to which rotamer. However, with related unsymmetrical species of the form



belonging to each rotamer when unequally intense pairs of resonances were observed [14].

Unsymmetrical dialkylaminodiphenylboranes (Ph_2BNRR^1)

The assignments of the ^{13}C NMR of the two compounds studied are given in Table 1. In both compounds the resonance assigned to the *ortho* carbon atoms is observed as a pair of lines demonstrating p_π – p_π bonding in these compounds. In contrast, no useful information could be obtained from their

^1H NMR spectra due to the fact that the aromatic protons were observed as a single broad envelope.

Symmetrical dialkylaminodiphenylboranes (Ph_2BNR_2)

The ^{13}C NMR spectra were also recorded for four compounds in this class, Table 1, in order to compare these spectra with the aminodiphenylboranes.

Correlations of aromatic carbon resonances in alkyl- and dialkylaminodiphenylboranes

Para carbon resonances

Odom has postulated that the $-\text{BBR}_2$ group, and most other boryl groups, act as mesomeric acceptors while the $\text{B}(\text{NR}_2)_2$ group acts as a weak mesomeric donor [9]. For the compounds studied the ^{13}C resonances were observed in the region of 129 ppm, indicating a slight deshielding relative to benzene (128.3 ppm) in contrast to the values for the dialkylamino derivatives (126–127 ppm) which indicate a slight shielding relative to benzene. In the case of the latter systems it is likely that the dialkylamino group is twisted out of the plane. However in the alkylamino systems there is restricted rotation about the B–N bond, indicating relatively strong $p_\pi-p_\pi$ bonding, as is evident from the ^{13}C NMR spectra. This indicates that the B–N bond is planar and models show that the phenyl groups will be twisted out of the plane to accommodate the planarity of the B–N bond, thus reducing B–C $p_\pi-p_\pi$ bonding with the result that the *para* carbon atoms are not mesomerically shielded.

Ortho carbon resonances

The ^{13}C resonances for this series of compounds range, in chemical shift, from 130.8 to 135.7 ppm. It would be expected that the δ_c for the *ortho* resonances would parallel that for the *para* resonances if the mesomeric effect was the only factor affecting shielding of the *ortho* carbon atoms. However, while δ_c (*para*) is sensitive to the electronic nature of the boron substituents δ_c (*ortho*) is affected by the electronic nature of the boron substituents and other factors due to its proximity to boron. Consequently, as might be expected there appears to be no simple relationship between δ_c (*ortho*) and the nature of the boryl group. It is worth noting that in all cases studied the *ortho* carbon resonances are found to low field of the *para* carbon signals.

Meta carbon resonances

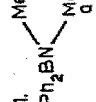
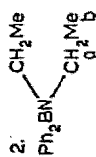
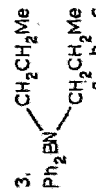
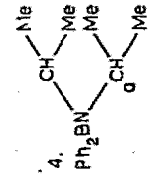
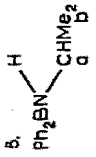
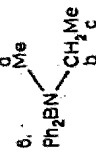
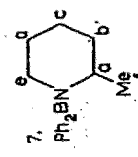
The chemical shifts range from 127.0 to 127.7 ppm, which is slightly deshielded relative to benzene. The narrow range indicates that the resonance is neither indicative of the nature of the boron substituents nor sensitive to mesomeric interactions of the boryl group with the phenyl group, as expected by analogy with other *meta*-substituted benzene derivatives [16].

C(1) resonances

The chemical shifts range from 140.2 to 146.2 ppm. A comparison of the values of the dialkylamino derivatives with the alkylamino derivatives indicate considerable deshielding of the C(1) in the case of the former compounds while

TABLE 1

¹³C NMR ASSIGNMENTS FOR SOME ALKYLAMINO- AND DIALKYLAMINODIPHENYLBORANES

Compound ^a	$\nu(\text{N-H})$ (cm^{-1})	C(1)	δ	m	p	a	b	c	d	e	f
1. 	—	143.1, —	133.4, 133.1	127.4, 127.2	127.4, 127.2	41.7, 41.5					
2. 	—	143.7 —	131.9, 131.8	127.4, 127.3	127.4, 127.3	42.6 42.5	15.6, 15.5				
3. 	—	144.2 —	132.4, 132.0	127.7, 127.4	127.7, 127.4	50.3, 50.1	22.9, 22.5	11.5, 11.2			
4. 	—	146.2	130.8, 130.4	127.4, 127.2	126.5, 126.2	49.1, 48.9	24.5, 24.3				
5. 	3370	140.4 0	133.5, 132.7 20	127.7, 127.4 8	129.4 0	45.0 0	26.5 0				
6. 		143.2	132.9, 132.1 18	127.3 0	127.3 0	47.5 0	37.6 0	14.9 0			
7. 		143.8 0	132.5, 132.0 12	127.3 0	127.3 0	50.1 0	32.2 0	19.3 0	28.6 0	43.0 0	18.2 0

8.		3385	140.5, 140.3 6	133.5, 133.0 12	127.5, 127.3 5	129.2	43.9	35.4	19.8	13.8
9.		3365	140.5, 140.4 3	133.5, 132.6 23	127.7, 127.5 5	129.5	49.9	31.9	23.7	10.2
10.		3375	141.2, 140.3 23	132.9, 131.5 35	127.5, 127.0 13	129.2	51.2	33.0		
11.		3400	140.5 0	133.5, 133.0 13	127.7, 127.3 10	129.4	55.9	32.2	27.1	
12.		3270	140.2, 137.4 70	135.7, 133.3 63	127.5, 127.0 13	129.0	50.7			
13.		3370	140.7 0	133.6, 133.0 15	127.7 0	129.4	52.2	37.1	25.5	25.1
14.		3340	141.4, 140.5 23	133.9, 132.3 40	127.7 13	129.5	1.81			

a The chemical shift (in ppm) of a signal arising from a particular carbon atom in one rotamer is given first followed by the chemical shift of the same nucleus in the other rotamer and the isomer shift, $\Delta\nu$, in Hz.

the opposite trend was observed for the $\delta(^{13}\text{C})$ *para* resonances.

	Ph_2BNR_2	Ph_2NHR
$\delta^{13}\text{C}(\text{C}(-1))$	143–146 ppm	140.5–142 ppm
$\delta^{13}\text{C}(\textit{para})$	~127.3 ppm	129.2–130 ppm

The C(1) becomes progressively deshielded as the steric hindrance of the amino group increases while the *para* carbons show the reverse trend (Table 1). This trend might be interpreted in the following way. In alkylaminophenylboranes strong $p_\pi-p_\pi$ bonding is indicated in the ^{13}C NMR spectra recorded at ambient temperature. Models indicate that since the B–NHR group must approach planarity for such π bonding the phenyl groups are probably twisted out of the plane. This results in the deshielding of the C(1) by boron being partly offset by the efficient back donation from nitrogen. In contrast, in the case of the dialkylaminophenylboranes the C(1) are relatively more deshielded and become progressively more deshielded as the NR_2 group becomes more bulky. In these cases the bulky amino group is probably twisted out of the plane and back donation from nitrogen thereby reduced. The increased electron deficiency on boron is thus relieved by inductive withdrawal from the C(1) which is not offset by back donation from nitrogen or the phenyl groups.

General trends of *para* carbon resonances

In a study of the ^{13}C spectra of a series of phenylboranes Odom suggested that there was a good correlation between $\delta^{13}\text{C}(\textit{para})$ with the electronic nature of the substituents on boron [17]. Table 2 lists chemical shifts for the *para* carbon resonances for a series of diphenylboranes. The $\delta^{13}\text{C}(\textit{para})$ value for Ph_2BCl appears to be low. This could be accounted for by the steric hindrance caused by the two phenyl groups which are twisted out of the plane hence reducing B–C $p_\pi-p_\pi$ bonding. Alternatively it could be argued that with two phenyl groups acting as π donors to boron the mesomeric deshielding is reduced compared to the phenylboranes. These views are supported by the relatively high shielding of the *para* carbon atoms in triphenylborane (131.1 ppm). In this compound twisting of the phenyl rings out of the C_3B plane greatly reduces the B–C $p_\pi-p_\pi$ bonding [15]. Alternatively, it could be argued that as the number of phenyl substituents on boron decreases the demand placed on each remaining phenyl group for π electron density increases resulting in increased mesomeric withdrawal from the *para* position. Similar arguments have been proposed in the rationalisation of the deshielding of the C_β atom in the series $\text{Cl}_2\text{BCH}=\text{CH}_2$, $\text{ClB}(\text{CH}=\text{CH}_2)_2$ and $\text{B}(\text{CH}=\text{CH}_2)_3$ [10].

Generally, the $\delta^{13}\text{C}(\textit{para})$ values do not change much when the alkyl group in compounds of the type Ph_2BNR_2 , Ph_2BOR and Ph_2BSR is varied. However,

TABLE 2

para CARBON RESONANCES FOR A SERIES OF DIPHENYLBORANES

Compound	Ph_2BBr	Ph_2BCl	Ph_2BOEt	Ph_2BSEt	PhH	Ph_2BNEt_2
$\delta^{13}\text{C}(\textit{para})$ (ppm)	133.4	132.9	130.0	130.2	128.5	127.3

when the alkyl group is very hindered a slight shielding of the *para* carbon atom results e.g. $\text{Ph}_2\text{BNPr-}i_2$ (126.2 ppm) of Ph_2BNMe_2 (127.2 ppm). This implies a twisting of the amino group out of the plane resulting in enhancement of B—C p_π — p_π bonding.

Experimental

Preparation of t-butylaminodiphenylborane

Chlorodiphenylborane (8.02 g, 0.04 mol) was dissolved in benzene and the mixture cooled in an ice bath. *t*-Butylamine (2.92 g, 0.04 mol), dissolved in benzene, was added dropwise with stirring, after which the mixture was allowed to attain room temperature. Triethylamine (4.05 g, 0.04 mol) dissolved in benzene was added slowly to the mixture and after the addition was complete the mixture was refluxed for three hours. After cooling triethylammonium chloride (5.5 g, 100%) was removed by filtration and after removal of the benzene under vacuum the residue on distillation under reduced pressure afforded *t*-butylaminodiphenylborane (6.16 g, 65%), b.p. 120°C/0.2 mmHg. (Found: C, 81.1; H, 8.2; N, 5.9. $\text{C}_{16}\text{H}_{20}\text{NB}$ calcd.: C, 81.0; H, 8.4; N, 5.9%).

Preparation of i-propylaminodiphenylborane

i-Propylamine (2.95 g, 0.05 mol) was dissolved in petroleum ether (b.p. 40–60°C) and the solution cooled in an ice bath. Chlorodiphenylborane (4.01 g, 0.02 mol), dissolved in petroleum ether, was added dropwise with stirring and after addition was complete the mixture was refluxed for three hours. On cooling *i*-propylammonium chloride (1.89 g, 100%) was filtered off and, on removal of the benzene under vacuum, the residue on distillation under reduced pressure afforded *i*-propylaminodiphenylborane (2.90 g, 65%), b.p. 105°C/0.05 mmHg. (Found: C, 81.0; H, 9.0; N, 6.2. $\text{C}_{15}\text{H}_{16}\text{NB}$ calcd.: C, 80.7; H, 8.1; N, 6.3%).

Preparation of trimethylsilylaminodiphenylborane

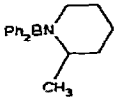
Bis(trimethylsilyl)amine (3.22 g, 0.02 mol) was dissolved in benzene. Chlorodiphenylborane (4.01 g, 0.02 mol) was slowly added and the resulting mixture refluxed for three hours. The solvent was removed under vacuum and the residue on distillation under reduced pressure afforded trimethylsilylaminodiphenylborane (2.53 g, 50.0%) b.p. 110°C/0.1 mmHg. The compound was characterised by a precise mass determination of the molecular ion (Found: 253.146683. $\text{C}_{15}\text{H}_{20}\text{NBSi}$ calcd.: 253.145802; error 3.48 ppm).

Table 3 records the analysis details and boiling points of the aminodiphenylboranes which were synthesised by either of the first two methods. Where no reference is given in the table it can be assumed that the compound was not previously reported in the literature.

NMR spectra were recorded on a JEOL-PS-100 NMR spectrometer. The ^1H NMR spectra were recorded in the continuous wave mode while ^{13}C NMR were recorded using the F.T. mode. Tetramethylsilane was used as an internal standard and the compounds were studied as solutions in CCl_4 , CDCl_3 or as neat samples. Chemical shifts quoted are correct to ± 0.05 ppm. An internal DMSO capillary lock was used when measuring the ^{13}C NMR spectra of neat samples

TABLE 3

PROPERTIES OF SOME ALKYLAMINO- AND DIALKYLAMINODIPHENYLBORANES

Compound	Yield (%)	B.p. (°C/mmHg)	Analysis Found (calcd.) (%)			Ref.	Ref. b.p. (°C/mmHg)
			C	H	N		
Ph ₂ BNMe ₂	80	100/0.1				19	98/0.1
Ph ₂ BNEt ₂	70	100/0.1				20	104/0.1
Ph ₂ BNPr ₂ ⁿ	65	120/0.1	80.3 (81.5)	9.0 (9.1)	5.2 (5.3)		
Ph ₂ BNPr ₂ ⁱ	65	120/0.1				21	124/4
Ph ₂ BNPr ₂ ⁱ	65	105/0.5	81.0 (80.7)	9.0 (8.1)	6.2 (6.2)	—	—
Ph ₂ BNHBu ⁿ	65	120/0.2	80.3 (81.0)	8.0 (8.4)	5.6 (5.9)	—	—
Ph ₂ BNHBu ^s	65	120/0.2	80.9 (81.0)	7.1 (8.4)	5.8 (5.9)	—	—
Ph ₂ BNHBu ^t	65	120/0.2	81.1 (81.0)	8.2 (8.4)	5.9 (5.9)	18	108/0.5
Ph ₂ BNHneopent ^a	55	125/0.1				—	—
Ph ₂ BNHC ₆ H ₁₁	55	160/0.1	80.9 (82.1)	7.9 (8.4)	5.2 (5.6)	—	—
Ph ₂ BNHNMe ₂	65	130/0.05	75.3 (75.0)	7.5 (7.6)	11.6 (12.5)	—	—
Ph ₂ BNHSiMe ₃ ^b	50	110/0.1				—	—
Ph ₂ BNMeEt	65	120/0.1	81.7 (80.7)	8.0 (8.1)	6.2 (6.3)	—	—
	60	120/0.1	81.2 (82.1)	8.4 (8.4)	5.0 (5.3)	—	—

^a Characterised by precise mass determination on molecular ion (Found: 251.1833406. C₁₇H₂₃NB calcd.: 251.1845220; error 1.7 ppm). ^b Characterised by precise mass determination on molecular ion, see text.

and the temperature of the sample was varied by passing a stream of heated air or cold nitrogen over the probe.

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