Methylaminodiphenylborane – Application of $^{11}$B, $^{13}$C, $^{14}$N, $^{15}$N NMR

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BC(pp)$\pi$ Interactions, NMR Spectra, Rotation about the BN bond

$^{11}$B, $^{13}$C, $^{14}$N, $^{15}$N NMR is used to study methylaminodiphenylborane (I). Compound I can be regarded as a model compound for studying BN(pp)$\pi$ interactions, for determining the barrier to rotation about the B–N bond and for the application of natural abundance $^{15}$N NMR to boron-nitrogen chemistry. The $^{13}$C NMR of I shows a large splitting of the $^{13}$C para resonances (in contrast to reports on similar compounds in the literature) as a consequence of hindered rotation about the BN bond. The difference in the $^{13}$C para nuclear shielding indicates different mesomeric interactions between the trigonal boron atom and the two phenyl groups.

![Diagram of methylaminodiphenylborane (I)](image)

The presence of BC(pp)$\pi$ interactions in addition to BN(pp)$\pi$ bonding in aminophenylboranes is still a matter of debate. Important information pertinent to this problem can be derived from $^{11}$B, $^{13}$C and $^{14}$N, $^{15}$N NMR [2]. This note reports $^{11}$B, $^{13}$C, $^{14}$N and $^{15}$N NMR data of methylaminodiphenylborane (I):

<table>
<thead>
<tr>
<th></th>
<th>(i)</th>
<th>(o)</th>
<th>(m)</th>
<th>(p)</th>
<th>NCH$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{11}$B</td>
<td>139.5</td>
<td>140.2</td>
<td>133.5</td>
<td>127.5</td>
<td>127.9</td>
</tr>
<tr>
<td>$^{13}$C</td>
<td>41.5</td>
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<tr>
<td>$^{14}$N</td>
<td>-285.7</td>
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$^{11}$B NMR

The $^{11}$B chemical shift, $\delta^{11}$B 41.5, does not change between 0 °C to 60 °C, indicating the monomeric nature of I in solution. The comparison with $\delta^{11}$B values for other diphenylboranes [2, 3] suggests significant BN(pp)$\pi$ interactions.

$^{13}$C NMR

The $^{13}$C NMR spectra of many aminodiphenylboranes, (C$_6$H$_5$)$_2$BNRR' [4–8], show that there is restricted rotation about the BN bond. Although this corroborates the interpretation of the $^{11}$B nuclear shielding, the contribution of steric hindrance to the barrier to rotation about the BN-bond remains unde-

fined. Furthermore, it is stated in reference [7] that all compounds studied with R = H and R' = alkyl, Si(CH$_3$)$_3$, N(CH$_3$)$_2$ give rise only to a single $^{13}$C para resonance. However, the $^{13}$C ortho and $^{13}$C meta resonances are always split into two signals. This is surprising because the $^{13}$C meta resonances are, in general, very sensitive to mesomeric interactions. These BC(pp)$\pi$ interactions should be noticeable especially in alkylaminodiphenylboranes such as I where at least one phenyl group (trans to alkyl) experiences a minimum of steric repulsion from the NH site. In the $^{13}$C NMR spectra shown in reference [7] an additional $^{13}$C para resonance may be hidden underneath the $^{13}$C meta resonances. The $^{13}$C NMR spectrum of I (Fig. 1) clearly shows two $^{13}$C para resonances, one being close to the $^{13}$C meta resonances. The value $\Delta G_{\text{cal}}$ (25 °C) for the barrier to rotation about the BN bond in I can be evaluated to 60.0 ± 1 kJ/M [9]. From the data given [7] $\Delta G_{\text{cal}}$ (=180 °C) in (C$_6$H$_5$)$_2$BNH tert-C$_6$H$_5$ should be > 90 kJ/M which reflects part of the steric influence upon the energy of activation.

A tentative assignment of the $^{13}$C para resonances in I is based on $\delta^{13}$C para for (C$_6$H$_5$)$_2$B–N(CH$_3$)$_2$ (127.9 [4]). This suggests that the $^{13}$C para resonance of the phenyl group in cis-position to the NCH$_3$ group is observed at lower frequency (Fig. 1, (p')). The amount of BC(pp)$\pi$ interactions is determined by the average twist angle of the phenyl groups with the NBC$_2$ plane. It can be assumed that steric hindrance will be greater for the phenyl group in cis-position to the NCH$_3$ group than for the phenyl group in trans-position. Therefore, it is concluded that the deshielding of the $^{13}$C para nucleus in the latter results from BC(pp)$\pi$ interactions.
$^{14}$N, $^{15}$N NMR

Although modern NMR instrumentation enables fast measurement of $^{14}$N NMR spectra, widespread application of $^{14}$N NMR is hampered owing to efficient quadrupole induced relaxation of the $^{14}$N nucleus. Thus, the line widths of $^{14}$N resonances increase readily with increasing molecular weight in the case of unsymmetrical charge distribution around the quadrupolar $^{14}$N nucleus. This causes loss of fine structure arising from scalar spin-spin coupling and leads to low accuracy of the $\delta^{14}$N values (see Fig. 2). The alternative is natural abundance $^{15}$N NMR which has become more and more common in recent years, mainly as a result of various spin-polarization transfer techniques (INEPT [11, 12], DEPT [13]). In the case of aminoboranes the $^{15}$N resonances may be severely broadened owing to scalar $^{15}$N–$^{11}$B coupling [14]. $^{15}$N–$^{11}$B spin-spin coupling contributes to transverse relaxation (scalar relaxation of the second kind [15]). Considering the development of transverse $^{15}$N

![Fig. 1. 50.3 MHz $^{13}$C NMR ($^1$H-decoupled) of methylaminodiphenylborane (1) at $-40\,^\circ\text{C}$ in CDCl$_3$. The assignment of the $^{13}$C resonances is based on $^1$H-coupled spectra (to distinguish $^{13}$C$_{ortho}$ and $^{13}$C$_{meta}$ on integral intensities in $^1$H decoupled spectra with NOE suppression ($^{13}$C$_{para}$)). The very broad single $^{13}$C$_{ipso}$ resonance at room temperature is sharpened in a heteronuclear triple resonance experiment $^{13}$C($^1$H, $^1$B).](image1)

![Fig. 2. 14.4 MHz $^{14}$N NMR of methylaminodiphenylborane, 1, at 27–28 °C in CDCl$_3$. The enormous line width (≈1000 Hz) demonstrates the limited application of $^{14}$N NMR in this field of chemistry.](image2)
magnetization in the various polarization transfer pulse sequences, it appears that the basic INEPT pulse sequence [11] should give the best results. The quadrupolar relaxation time of the $^{11}$B nucleus is fairly short in phenylaminoboranes ($T_{Q(B)} = 1.3$ ms in 1, 10% CDCl$_3$ solution at 27–28 °C). Therefore, $J(^{15}$N$^{11}$B) is almost completely averaged $(2\pi \cdot J(^{15}$N$^{11}$B) \cdot T_{Q(B)} < 1$ [15]). Although the $^{15}$N NMR spectrum in Fig. 3 shows some residual broadening, it can be recorded within ~2 h using the basic INEPT pulse sequence [11]. The application of refocused INEPT [12] or DEPT [13] requires more spectrometer time owing to less efficient polarization transfer because of the short transverse relaxation time $T_2(^{15}$N).

The $\delta^{15}$N value (−285.7) of 1 falls into the range found for aminodiorganylboranes [16], and is typical for delocalization of the nitrogen lone electron pair [17]. The value $J(^{15}$N$^{1}$H) (79.5 Hz) in 1 is similar to values found for borazine (79 Hz [18]) or aminodimethylborane (80.0 Hz [19]).

These observations should encourage the application of natural abundance $^{15}$N NMR measurements to boron nitrogen compounds, in particular to those of greater molecular weight. The latter, in general, give broad unresolved $^{11}$B resonances providing very little information on the structure of the compounds under investigation. However, the rapid quadrupolar relaxation of the $^{11}$B nucleus ensures efficient averaging of the scalar coupling $J(^{15}$N$^{11}$B) which improves the signal to noise ratio in the $^{15}$N NMR spectra.

**Experimental**

All NMR spectra have been recorded in 10 mm o.d. tubes as 10% solutions (weight/volume) in CDCl$_3$ using a BRUKER WP 200 NMR spectrometer equipped with a multinuclear unit. Chemical shifts are given with respect to external BF$_3$-O(C$_2$H$_5$)$_2$ ($\delta^{11}$B), (CH$_3$)$_4$Si ($\delta^{13}$C CDCl$_3$ = 77.0) and 0.1 M CH$_3$NO$_2$ in CDCl$_3$ ($\delta^{15}$N, $\Xi_{15}$N = 10136719 Hz).

Methylaminodiphenylborane (1) has been prepared according to the literature [20]. Compound 1 is obtained in 45% yield by distillation (b.p. 90–93 °C/10⁻² mm Hg) as a viscous colourless liquid. This turns slowly into a colourless crystalline solid (m.p. 60–63 °C), which becomes pale yellow after several months. The solid dissolves readily in CHCl$_3$ as the monomer 1 ($^{11}$B NMR, osmometric molecular weight measurement). $^1$H NMR (200 MHz) in CDCl$_3$ (5%): $^1$H 2.96 (d, $J_{HH}$ 6.1 Hz, 3H) NCH$_3$; 4.8 (q, breit, 1H) NH; 7.30–7.75 (m, 10H) C$_6$H$_5$.

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