

**NOTIZEN**

\[ ^{15}\text{N} \text{ NMR Study of Tris(dimethylamino)phosphine Derivatives: (Me}_2\text{N})_3\text{PSe, (Me}_2\text{N})_3\text{PTe and (Me}_2\text{N})_3\text{PBH}_3 \]

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Aminophosphines, \(^{15}\text{N} \text{ NMR Spectra, Relaxation}

The title compounds have been studied by \(^{11}\text{B}, \(^{15}\text{N}, \(^{31}\text{P}, \(^{77}\text{Se} \text{ and } ^{125}\text{Te NMR spectroscopy (6-values, coupling, constants). The } ^{15}\text{N relaxation is dominated by } ^{15}\text{N}-^1\text{H dipolar interactions whereas nuclear screening anisotropy controls the } ^{125}\text{Te relaxation.}}

Nuclear magnetic resonance (NMR) parameters yield important information on the bonding situation when the co-ordination number of phosphorus increases from three to four. In amino-phosphorus compounds \(^{15}\text{N} \text{ NMR data [1]} \text{ may be helpful since both sign and magnitude of the indirect nuclear spin-spin coupling constant depend upon the phosphorus oxidation state and upon the hybridization of phosphorus as induced by various substituents [2]. Furthermore, NMR data of other nuclei linked to the phosphorus atom may provide additional information in this respect. We have now studied three derivatives of tris(dimethylamino)phosphine (1) \([3—5], \text{ namely the compounds 4, 5 and 7 by means of } ^{11}\text{B}, \(^{15}\text{N}, \(^{31}\text{P}, \(^{77}\text{Se} \text{ and } ^{125}\text{Te NMR spectra. The NMR parameters are given in the Table together with the data for the other compounds in this series.}}

\[
\begin{array}{cccccccc}
\text{X} & \text{lonepair} O & \text{S} & \text{Se} & \text{Te} & \text{NET} & \text{BH}_3 \\
(\text{Me}_2\text{N})_3\text{P—X} & \text{Nr} & 1 & 2 & 3 & 4 & 5 & 6 & 7 \\
\end{array}
\]

The \(^{11}\text{B}, \(^{15}\text{N}, \(^{31}\text{P}, \(^{77}\text{Se} \text{ and } ^{125}\text{Te NMR spectra were recorded using a BRUKER WP 200 spectrometer equipped with a multinuclear unit. The } ^{15}\text{N NMR spectra in natural abundance have been obtained with } ^1\text{H broad band decoupling (ca. 2000 scans, pulse angle ca. 18°, acquisition time 8 s, concentrated solutions in } \text{C}_6\text{H}_6 \text{ or toluene/C}_6\text{D}_6 \text{.}}

In the compounds studied \(^{15}\text{N—}^1\text{H dipolar interactions dominate the relaxation of the } ^{15}\text{N nucleus and the resulting negative nuclear Overhauser enhancement factor } \eta \text{ is sufficiently large (} \eta_{\text{max}}(^{15}\text{N}) = -4.93). The application of the refocused INEPT pulse sequence [6a, b] also gave reasonable results assuming a coupling constant } J(^{15}\text{N}^1\text{H}) \text{ of ca. 1 Hz. However, in case of compound 7 no } ^{15}\text{N-resonance could be found using this method. From the normal } ^{15}\text{N}^1\text{H spectrum it was evident that the } ^{15}\text{N resonance for 7 is broadened by partially relaxed scalar coupling } ^{15}\text{N—P—}^1\text{B}, \text{ indicating a shortening of } \text{T}_2(^{15}\text{N}). \text{ Considering this and the fairly long delay time in the refocused INEPT pulse sequence owing to the small value } J(^{15}\text{N}^1\text{H}) \text{ it is understandable that the polarization transfer is ineffective. This also explains our failure to obtain good results with the DEPT sequence [6c] for which the delay times are even longer.}

The line width of the } ^{125}\text{Te resonance of compound 5 was found to be } 85 \pm 5 \text{ Hz at } 28 ^\circ \text{C. The measurement was repeated at a field strength } B_0 \text{ of 2.11 T (JEOL FX 900Q) and a line width of } 20 \pm 3 \text{ Hz was observed. These observations strongly suggest that at both field strengths the } ^{125}\text{Te relaxation rate is dominated by nuclear screening anisotropy: this process depends on } B_0^2 \text{ and the ratio of the line widths (4.25) is close to the ratio of the values for } B_0^2 \text{ (4.90). In contrast the tellurium relaxation in dimethyltelluride was found to be dominated entirely by spin-rotation interaction at } B_0 = 2.11 \text{ T and at } B_0 = 5.86 \text{ T [7].}

The linewidth of the } ^{77}\text{Se resonance (4.7 T) in compound 4 is only } ca. \text{ 4 Hz. Comparison with line width data obtained at } B_0 = 2.11 \text{ T are not meaningful because the position of the } ^{77}\text{Se resonance is significantly affected by small changes in the probe temperature.}

A positive sign has been found for } J(^{31}\text{P}^{15}\text{N}) \text{ in compound 1 [3] (the reduced coupling constant } K(^{31}\text{P}^{15}\text{N}) = 4 \cdot \pi / \hbar \cdot J(^{31}\text{P}^{15}\text{N}) \cdot (\gamma_{^{15}\text{N}}^2/\gamma_{^{31}\text{P}}^2)^{-1} \text{ is negative owing to the negative sign of } \gamma_{^{15}\text{N}}. \text{ There are increasingly positive contributions to } K(^{31}\text{P}^{15}\text{N}) \text{ starting from compound 1 to 7, 5, 4, 3, 2, 6. Assuming the dominance of the Fermi contact term [8] the pattern of the values } J(^{31}\text{P}^{15}\text{N}) \text{ can be explained qualitatively in terms of increasing s-electron density in the P—N bond. Strongly electronegative groups X (O, S, NR) are expected to induce greater s-character in the P—N bond as compared to the more electropositive and readily polarizable groups X (BH}_3, \text{ Se, Te). In addition to these effects negative contributions to } K(^{31}\text{P}^{15}\text{N}) \text{ can be attributed to the presence of the lone electron pairs at the nitrogen atoms.}

In contrast to } K(^{31}\text{P}^{13}\text{C}) [9] the increase in the coordination number of phosphorus from three to four does not necessarily involve a positive sign of } K(^{31}\text{P}^{15}\text{N}). \text{ However, the measurement of } J(^{31}\text{P}^{15}\text{N})
Table. Chemical shifts $^3$ and coupling constants [Hz] of tris(dimethylamino)phosphine derivatives.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\delta^{31}P$</th>
<th>$\delta^{15}N$</th>
<th>$J^{(31}P^{31}N)$</th>
<th>$J^{(31}P^{31}E)$</th>
<th>$J^{(31}P^{31}E)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>122.0</td>
<td>-345.9</td>
<td>(+) 159.4</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>23.4</td>
<td>-357.1</td>
<td>(-) 26.9</td>
<td>(+) 245.0</td>
<td>73.0</td>
</tr>
<tr>
<td>3</td>
<td>81.4</td>
<td>-333.1</td>
<td>(-) 6.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>84.1</td>
<td>-343.0</td>
<td>(+) 5.1</td>
<td>(-) 812.0</td>
<td>-366.7</td>
</tr>
<tr>
<td>5</td>
<td>60.5</td>
<td>-347.1</td>
<td>(+) 13.2</td>
<td>(+) 2110.0</td>
<td>504.0</td>
</tr>
<tr>
<td>6</td>
<td>21.5</td>
<td>-360.9</td>
<td>(-) 32.7</td>
<td>(+) 29.0</td>
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<tr>
<td>7</td>
<td>106.0</td>
<td>-342.3</td>
<td>(+) 15.4</td>
<td>(+) 98.0</td>
<td>-42.2</td>
</tr>
</tbody>
</table>

$^a$ $\delta$ Values relative to BF$_3$−OEt (1B), 0.1 M CH$_3$NO$_2$ in CDC$_3$, $\Xi^{15}N = 10,136,719$ Hz (1N), H$_2$O ($^{17}O$), 85% H$_3$PO$_4$ ($^{31}P$), Me$_2$Se ($^{77}Se$), Me$_2$Te ($^{125}Te$). all external; positive signs denote shifts towards higher frequencies; 50 to 60% solutions (W/V) in CD$_3$ and toluene/CD$_2$ (5); in 10 mm o.d. tubes at 28 °C.


$^c$ Ref. [4] quotes $\delta^{15}N = -349.4$ relative to NO$_2^−$ and $J^{(31}P^{31}N)$ 60.1 Hz for a neat sample.

$^d$ Ref. [3] gives $J^{(31}P^{31}N) = 59.1$ 90% solution in C$_6$D$_{18}$.

$^e$ Ref. [1], p. 171, relative to neat CH$_3$NO$_2$.

$^f$ Ref. [3].


$^i$ $\delta^{77}Se$ $\pm 360$, $J^{(77}Se^{31}P)$ $\pm 805$ Hz in CH$_2$Cl$_2$, Ref. [12].

$^j$ Preparation and $J^{(125}Te^{31}P)$ (2045 Hz in CH$_2$Cl$_2$, 35 °C) Ref. [13].

$^k$ Ref. [5], $\delta^{15}N$ relative to neat CH$_3$NO$_2$ (presumable).


in 4, 5, and 7 shows that the sign of $J^{(31}P^{31}N)$ in 2, 3 and 6 is negative (Kr($^{31}P^{31}N$) is positive) in agreement with the trend of the $J^{(31}P^{31}N)$ values in the compounds Me$_2$P(X)$_2$NHPH [2]. Although there is no obvious relationship between the values $J^{(31}P^{31}N)$ and $\delta^{15}N$ the comparatively large range of the $\delta^{15}N$ values shows that the P−N bond is greatly affected by different groups X. There appears to be a crude relationship between $\delta^{31}P$ and $J^{(31}P^{31}N)$ which might be improved if the screening constant of the $^{31}P$ nucleus were corrected for the shielding effect exerted by heavy nuclei like tellurium [10].

The coupling constants $J^{(31}P^{31}B)$ (7) [11], $J^{(77}Se^{31}P)$ (4) [12], $J^{(125}Te^{31}P)$ (5) [13] and the $\delta^{13}B$ (11), $\delta^{77}Se$ (12) values agree with data from the literature. The value $J^{(125}Te^{31}P)$ (5) is found in the expected range if the data $J^{(77}Se^{31}P)$ in R$_2$PSe (ca. 700 Hz) and $J^{(125}Te^{31}P)$ in R$_2$PTE (ca. 1700 Hz [14,15]) serve for comparison. Similarly $\delta^{125}Te$ (5) and $\delta^{77}Se$ (4) fit the linear relationship observed for the isotropic shielding of both nuclei [16].

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