The Nuclear Magnetic Resonance Spectra of Geometrical Isomers of 2,4-Difluoro-1,3-di-t-butylcyclophosph(III)azane

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A new synthetic method for the preparation of the geometrical isomers of (FPNBu')2 by amine elimination from Me2N–P(F)–NBu' is described.

The 13C, 19F, and 31P NMR investigations lead to new structural assignments.

Although alkyl [1], amino [2-4], and alkoxy [5] derivatives of cyclophosph(III)azanes (I) are often obtained as mixtures of cis- and trans-isomers, only one isomer of each of the halogeno derivatives (I) (X = F [6], Cl [7], and Br [8]) has been isolated.

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In the solid state (I) (X = Cl) has a cis-structure (2), and it has been assumed that the same structure is obtained for the analogous bromide, (I) (X = Br) [8].

It seems very likely that the cis-structures also exist in solution. In this connection, the 19F and 31P NMR data of the fluoride (I) (X = F) are particularly interesting, since the spectra constitute an example of an AA'XX' spin system from which P..P, F..F and other spin couplings can, in principle, be obtained.

It has been suggested that the F..F coupling in particular reflects the geometrical arrangement of the fluorine atoms [9]. Spin couplings of ca. 95 and 30 Hz were first assigned to 4J(F,F) and 4J(F,F) respectively. Unfortunately, the analysis does not distinguish between J(AA') and J(XX'), and the earlier assignment [5] was reversed as a result of comparisons with data obtained for other fluoro-cyclophosph(III)azanes. This revision is consistent with the finding [10] that 4J(F,P) is also relatively large (53 Hz) in a platinum complex of (I) (X = F). The larger coupling has since been assigned to 4J(F,P) but the authors [11] appeared to be unaware of previous work in the area.

It has now been found that a mixture of geometrical isomers (2) and (3) can be obtained by the following reaction sequence:

\[
\text{Me}_2\text{N–PF}_2 + \text{LiBu}^\prime(\text{SiMe}_3) \rightarrow \text{LiF} \quad 120 \degree C
\]

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The major isomer has 19F and 31P NMR shifts similar to those previously reported [6, 9]. On standing at ambient temperature the proportion of the major isomer slowly increased. The proton-decoupled 19F and 31P NMR spectra of both isomers were analysed and the results are shown in the Table.

It can be deduced by inspection that 1J(PF) (negative [12]) and 3J(PF) are of opposite sign in both isomers. The relative signs of 2J(PF) + 4J(FP) and 1J(PF) + 3J(FP) were established by a series of 31P–(19F) double resonance experiments. These experiment confirmed previous findings [9] for the major isomer (Table), and showed that these combinations of spin couplings were of opposite sign in the minor isomer. The combinations [2J(PF) + 4J(FP)] and [3J(PF) − J(FP)] could not be distinguished in the double resonance experiments on the minor isomer as the 1.0 Hz splitting that was observed in the 19F spectrum was not resolved in the 31P spectrum. Hence the sign of the smaller (1.0 Hz) coupling could not be obtained, although the 75.3 Hz coupling in the minor isomer was shown to be positive.

Comparison of 13C and 31P NMR chemical shifts and PNC spin couplings for the two isomers with those of cyclophosph(III)azanes of known structure [1-5, 13, 14] are consistent with the assignment of a cis-structure to the isomer with 3J < 0 as in previous work. The fact that 2J(PF) is generally small (< 20 Hz) and negative for some trans-isomers of cyclophosph(III)azanes [9], indicates that the relatively large coupling of + 75.3 Hz must be assigned to 1J(FP). Thus 1J(PF) (= +94.4 Hz) in the cis-isomer [2] is not necessarily dominated by a trough-space interaction [9]. Support for this viewpoint comes from the measurement of 1J(PF) in the trans (2-trans-4-cis-6) isomer of (FPNEt)2 where these couplings all lie in the range 10–20 Hz [15].

There appears to be no doubt that the cis-isomer of these halogeno-cyclophosph(III)azanes are thermodynamically favoured over the analogous
Table. $^{13}$C, $^{19}$F, and $^{31}$P NMR data.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\delta$P</th>
<th>$\delta$F</th>
<th>$\delta$NC</th>
<th>$^1$J(PF)</th>
<th>$^3$J(PF')</th>
<th>$^2$J(PP')</th>
<th>$^4$J(FF')</th>
<th>$^2$J(PC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 (X = F)</td>
<td>165.5</td>
<td>-23.4</td>
<td>51.6$^b$</td>
<td>-1180.6</td>
<td>+22.1</td>
<td>+29.3</td>
<td>+94.0</td>
<td>9.6$^d$</td>
</tr>
<tr>
<td>3 (X = F)</td>
<td>247.9</td>
<td>-36.4</td>
<td>51.5$^c$</td>
<td>-1171.3</td>
<td>+22.1</td>
<td>+29.3</td>
<td>+94.0</td>
<td>6.3$^e$</td>
</tr>
</tbody>
</table>

$^a$ Obtained from CDCl₃ solutions at ambient temperature. References were TMS ($^{13}$C), CCl₃F ($^{19}$F), and H₃PO₄ ($^{31}$P); downfield shifts are positive. Spectra were obtained on a Varian XL-100 NMR spectrometer in the pulsed Fourier Transform mode, with proton-noise decoupling except for the $^{31}$P-$^{19}$F double resonance experiments. Spin couplings are in Hz (for the AA'XX' spectra, measured from the $^{19}$F NMR data).

Experimental

The usual precautions in handling air and moisture sensitive compounds were observed.

I. N,N-t-butyl(trimethylsilyl)amino-N',N'-dimethylaminodifluorophosphane (4)

49.8 g (330 mmoles) Lithium-t-butyl(trimethylsilyl)amide [16] in 200 ml diethylether were added slowly to 40.0 g (354 mmoles) N,N-dimethylaminodifluorophosphane [17] in 100 ml diethylether. After stirring under reflux (about 1 h) the solvent was evaporated. Vacuum distillation of the residue yields 54.2 g (69%) (4).


II. 2,4-Difluoro-1,3-di-t-butylcyclodiphosph(III)azanes (2, 3)

23.8 g (100 mmoles) (4) were pyrolised 2 h at 110 °C. Volatile products were condensed (−78 °C) and sublimed again (40 °C/0.05 Torr). Yield: 4.8 g (40%).


MS: m/e = 242M⁺ (35%), 227 M⁺-Me (94%)... 106 Me₂NCNPF (100%)...