The ^{31}P Chemical Shift of Phosphorus Pentafluoride

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Summary The δ_P value of PF_5 employed previously has been shown to be in error: the implications of this finding are discussed.

THE ^{31}P chemical shift of phosphorus pentafluoride is significant, both because it concerns one of the simplest inorganic phosphorus compounds and because of its relationship to its substituted derivatives, the fluorophosphoranes.[1] For these compounds a characteristic upward trend in δ_P has been found, as the electronegativity of the equatorial substituents in the trigonal bipyramid increases. This trend appeared to be broken by the rather low δ_P value of $+35$ p.p.m. reported for PF_5.[2] This value which has been widely quoted in the secondary literature,[3] and has been employed in a theoretical study,[4] has now been found to be in error, and we report the correct δ_P value for PF_5 as $+ 80{\cdot}3$ p.p.m. The P–F coupling constant was found as 938 Hz., which is in reasonable accord with the value derived from the ^{19}F spectrum (see Table). The ^{31}P spectrum of PF_5 was measured on a liquid sample, in the -84 to $-90°$ region, at 24·288 MHz. The above values are the average of four independent runs.

It is apparent that the reported erroneous δ_P value must be ascribed to POF_3 which is known to be formed readily when PF_5 is handled in glass apparatus, as was the case in the original study.[2] In the present work a commercial sample of PF_5 was kept in a steel cylinder, and its contact with glass was kept to a minimum.

TABLE

Compound	δ_P (from 85% H_3PO_4)	J_{P-F} (Hz.)
PF_5	$+35{\cdot}1^a$	$1010^{a,b}$
		916^c
	$+80{\cdot}3^d$	$938^{b,d}$
POF_3	$+35{\cdot}5^a$	$1080^{a,b}$
		1058^e

[a] From ref. 2. [b] From ^{31}P n.m.r. [c] From ^{19}F n.m.r.[5]
[d] This work. [e] From ^{19}F n.m.r.[6]

A re-inspection of the original ^{31}P spectrum of what was then believed to be PF_5 showed that only four peaks of approximate intensity ratio 1 : 3 : 3 : 1 (as expected for POF_3) were observed. In the present work the required six peaks in the correct intensity ratio of 1 : 5 : 10 : 10 : 5 : 1 are observed for authentic PF_5.

The δ_P value of +80·3 p.p.m. is much more in line with the previously mentioned trend in δ_P of the fluorophosphoranes. It also requires the revision of the conclusion by Letcher and van Wazer[4] that PF_5 has the highest occupation of phosphorus π-orbitals of all PZ_5 compounds. It should be noted, finally, that the new δ_P value for PF_5 is virtually identical with that[7] of PCl_5 (+80 ± 2 p.p.m.).

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