Proton Exchange and Magnetic Nonequivalence in *N*-Isopropylaminophosphorus(V) Compounds

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It is well known that the methyl protons in an isopropyl-group adjacent to an asymmetric centre† may be magnetically nonequivalent as shown by their ^{1}H n.m.r. spectra.[1] The asymmetric centre may be a phosphorus atom bonded directly,[2,3] or through oxygen,[4] to the isopropyl-group. Nonequivalence was recently observed in di(isopropylamino)phenylphosphine, $PhP(NHPr^i)_2$,[5] and we now report on the origins of this effect in the corresponding sulphide, $PhP(S)(NHPr^i)_2$ (I), and selenide, $PhP(Se)(NHPr^i)_2$ (II).

In deuteriochloroform solution at 33° the isopropyl-methyl signals of these two compounds at *ca.* τ 8·9 consist of a doublet by coupling to the methine protons ($^3J_{H\text{-}C\text{-}C\text{-}H}$ ~6·0—6·5 c./sec.; $^4J_{P\text{-}N\text{-}C\text{-}C\text{-}H}$ and $^4J_{H\text{-}N\text{-}C\text{-}C\text{-}H}$ $\leqslant$0·5 c./sec.) which

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† Reference to an asymmetric centre at phosphorus will be taken to include molecules of the type, $R^1R^2P(NHPr^i)_2$, where the $R^1R^2P(NHPr^i)$ group has C_1 symmetry.

TABLE

Compound[a]	δ (c./sec.)[b]			τ (NH)		
	$CDCl_3$	$CDCl_3$–HCl	PO$(NMe_2)_3$	$CDCl_3$	$CDCl_3$–HCl[c]	PO$(NMe_2)_3$
PhP(S) (NHPr^i)$_2$ (I) (50°) ..	0·6	–	—	7·77	—	—
,, ..	1·5	0	6·6	7·75	7·34	5·29
,, (−60°) ..	6·5	–	—	7·75	—	—
PhP(Se)(NHPr^i)$_2$ (II) ..	3·2	0	6·2	7·66	5·81	5·23
Ph$_2$P(S)(NHPr^i)$_2$ (III) ..	0	–	0	7·74	—	3·95

[a] Compound (I) has been reported previously.[5] Good analytical figures were obtained for (II) and (III).

[b] The chemical shift between the isopropyl-methyl signals is quoted in c./sec. for convenience. Spectra were measured at 60 Mc./sec. and the sample temperature was 33° unless otherwise stated. Solutions were generally ~10% w./v. and dilution below this concentration did not affect δ by more than 0·2 c./sec.

[c] These shifts alter with HCl concentrations; no quantitative measurements of this factor were made.

is doubled again due to magnetic nonequivalence. However, chemically shifted methyl signals were not observed for compound (III) (Table) where an isopropylamino-group is replaced by a phenyl-group. In this case, the Ph$_2$P(S)- group contains a plane of symmetry. Similar observations have been made for isopropylphosphorus compounds.[2]

The magnitude of the nonequivalence (δ) in the spectrum of the sulphide (I) is temperature dependent (Table), indicating the presence of an exchange process of an intermediate rate on the n.m.r. time-scale at 33°. Coalescence is almost complete at 50°. This effect is unlikely to be the result of restricted rotation of the isopropyl-group relative to the phosphorus atom, since nonequivalence should persist even when rotation is fast (*cf.* ref. 4) by virtue of the asymmetric centre at phosphorus. A more likely explanation is that relatively high rates of inversion at the nitrogen atoms effectively average out the observed chemical shift differences. Assuming this to be correct, then changes in nitrogen inversion rates are paralleled by changes in proton exchange rates at this centre. Thus the NH signal of (I) at 33° is an exchange broadened ($W_{\frac{1}{2}}$‡ = 12 c./sec.) spin-coupled triplet at τ 7·75, where $^2J_{P\text{-}N\text{-}H} \sim {}^3J_{H\text{-}N\text{-}C\text{-}H} \sim 9$ c./sec., whereas at −60° it is a relatively sharp triplet ($W_{\frac{1}{2}} = 3$ c./sec.).

Further evidence for a correlation between the rate of proton exchange at nitrogen and δ comes from the effect of solvent on this parameter. In deuteriochloroform solution, δ is 1·5 c./sec. for the sulphide (I) and decreases to zero on introducing small quantities of dry hydrogen chloride into the solution. At the same time, the NH signal moves downfield and coalesces to a sharp singlet resonance ($W_{\frac{1}{2}} = 1$ c./sec.) as the acid concentration is increased. The methine proton signal also sharpens up under these conditions and may be recognised as two overlapping septets ($^3J_{P\text{-}N\text{-}C\text{-}H} = 11{\cdot}0$ c./sec.). Proton exchange rates such as those prevailing when small concentrations of hydrogen chloride are present are likely to be accompanied by a relatively high rate of nitrogen inversion. No protonated (I) or (II) could be isolated, but the presence of acid resulted in the formation of traces of isopropylamine hydrochloride by phosphorus–nitrogen bond cleavage. The value of δ was unaffected by the addition of comparable amounts of this salt to deuteriochloroform solutions of (I) and (II). The value of δ for (I) and (II) is relatively large in the basic solvent hexamethylphosphoramide, P(O)$(NMe_2)_3$, where conditions of very slow proton exchange exist. Thus the NH signals are fairly sharp triplets ($W_{\frac{1}{2}} = 4$ c./sec.) at *ca.* τ 5·3.

It appears that associative effects in the latter solvent are important in determining the magnitude of δ. However, weaker intermolecular association has the opposite effect. On increasing the concentration of (I) in deuteriochloroform (>20%) δ decreases, but a similar effect is not observed for (II). The behaviour of δ in the more basic oxide, PhP(O)(NHPr^i)$_2$, is different again and we are presently seeking to rationalise these differences in terms of the relative basicities of the compounds.

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‡ $W_{\frac{1}{2}}$ = line width at half peak height.

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