

891. *Phosphorus-Nitrogen Compounds. Part XV.¹ The ¹H Nuclear Magnetic Resonance and Infrared Spectra of Some Mononuclear Phosphorus(v) Compounds containing the P-NMe₂ Grouping*

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The ¹H n.m.r. spectra of a series of phosphorus(v) compounds, PXCl_{3-n}(NMe₂)_n (X = O or S), have been measured. Measurements were also made on some related compounds with the chlorine replaced by phenyl or amino groups. The effect of progressively replacing chlorine atoms by amino-, dimethylamino-, and phenyl groups is discussed in terms of chemical shifts and ³¹P-¹H coupling constants of the dimethylamino-groups. The infrared spectra of these compounds have been measured and their salient features are discussed.

THE number of proton environments and the magnitudes of the apparent * phosphorus-proton spin-spin coupling constants (J_{P-H}) observed in dimethylamino-derivatives of the phosphazenes has proved useful in the identification of geometrical and positional isomers.²⁻⁷ In order that the effects of increasing dimethylaminolysis at a quinquivalent phosphorus atom be more fully understood, a systematic study of the spectra of the series, PXCl_{3-n}(NMe₂)_n (X = O or S), has been undertaken.

Although the ¹H n.m.r. spectra of many organophosphorus compounds have been reported and discussed, *e.g.*, refs. 8-15, relatively little data exist for compounds containing the P-N-C-H grouping.¹⁰⁻¹²

The methyl proton signals of the compounds investigated all appear as doublets

* The apparent value of J_{P-H} in the phosphazenes is probably slightly different from the real value because of long-range proton-phosphorus coupling.

¹ Part XIV, B. W. Fitzsimmons, C. Hewlett, and R. A. Shaw, preceding Paper.

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⁶ J. H. Smalley, F. E. Dickson, and I. I. Bezman, *Inorg. Chem.*, 1964, **3**, 1780.

⁷ G. Ottmann, H. Agahigian, H. Hooks, G. D. Vickers, E. Kober, and R. Rätz, *Inorg. Chem.*, 1964, **3**, 753.

⁸ T. H. Siddall, *tert.*, and C. A. Prohaska, *J. Amer. Chem. Soc.*, 1962, **84**, 3467, and references therein.

⁹ J. B. Stothers and J. R. Robinson, *Canad. J. Chem.*, 1964, **42**, 967.

¹⁰ G. Martin and G. Mavel, *Compt. rend.*, 1961, **253**, 644.

¹¹ G. Martin and G. Mavel, *Compt. rend.*, 1962, **255**, 2095.

¹² G. Martin and A. Besnard, *Compt. rend.*, 1963, **257**, 898.

¹³ J. B. Hendrickson, M. L. Maddox, J. J. Sims, and H. D. Kaesz, *Tetrahedron*, 1964, **20**, 449.

¹⁴ F. Kaplan, G. Singh, and H. Zimmer, *J. Phys. Chem.*, 1963, **67**, 2509.

¹⁵ C. E. Griffin, *Tetrahedron*, 1964, **20**, 2399.

(methyl proton resonance split by coupling with phosphorus) centred in the region $\tau = 7.0-7.5$. There was no sign of broadening due to nitrogen quadrupole relaxation. As might be expected, increasing replacement of chlorine atoms by dimethylamino-groups moves the mean resonance position upfield, reflecting a greater electron density at the phosphorus atom. Substitution of a chlorine atom by a phenyl group also moves the dimethylamino-proton signal upfield, but, as with chlorine, the shift is not linear with the number of replacing groups. These results complement those already obtained from the phosphazenes where the shifts of the dimethylamino-protons in different environments can frequently be distinguished, depending on the nature of the second group attached to phosphorus.²⁻⁴ Less promising examples are the spectra of compounds containing both amino- and dimethylamino-groups, where replacement of one of the latter by one of the former affects but little the dimethylamino-proton shift. Replacement of oxygen by sulphur at the phosphorus atom moves mean resonance positions slightly downfield [compounds (I)—(VI)] the effect being greatest for the pair of monodimethylamino-derivatives $\text{POCl}_2\cdot\text{NMe}_2$ (I) and $\text{PSCl}_2\cdot\text{NMe}_2$ (IV). As noted by Martin and Mavel^{10,11} for compounds (I) and (IV) this effect is in the opposite sense to that expected from considerations of the electronegativities of oxygen and sulphur and is in contrast to results obtained for methylphosphine oxides and sulphides.¹³ This trend is not observed, however, when a phenyl group is present, *cf.* compounds (VII) and (IX). A survey of published chemical shifts^{9,12,13,16} for organophosphorus compounds containing P=S and P=O groups reveals a conflicting situation.

The measurement of phosphorus-proton coupling constants ($J_{\text{P-H}}$), which for the compounds reported here lie between 9 and 18 c./sec., is of interest. Theory indicates that the spin-spin coupling constant in the hydrogen molecule is determined mainly by the contact term,¹⁷ in which coupling occurs *via* electrons in *s*-orbitals. A similar relationship has been shown to hold for $^{13}\text{C}-^1\text{H}$ coupling over one bond^{18,19} where the percentage *s*-character of the hybrid atomic orbital on carbon is directly proportional to $J_{\text{C-H}}$. It is not unreasonable to assume that the hybridisation is very similar at the carbon atoms of the dimethylamino-group throughout the series of compounds in Table 1. The infrared spectra of these

TABLE 1
Proton magnetic resonance spectra * of dimethylamino-derivatives

Compound	τ	Lit.	$J_{\text{P-H}}$ (c./sec.)	Lit.	Ref.
(I) $\text{POCl}_2(\text{NMe}_2)$	7.13	7.14	15.8	15.3	12
(II) $\text{POCl}(\text{NMe}_2)_2$	7.29		13.0		
(III) $\text{PO}(\text{NMe}_2)_3$	7.40	7.44	9.5	9.25 †	12
(IV) $\text{PSCl}_2(\text{NMe}_2)$	6.98	7.00	17.2	17.8	11
(V) $\text{PSCl}(\text{NMe}_2)_2$	7.27		15.4		
(VI) $\text{PS}(\text{NMe}_2)_3$	7.38	7.38	11.3	10.8	11
(VII) $\text{POPh}(\text{NMe}_2)_2$	7.34		9.9		
(VIII) $\text{POPh}_2(\text{NMe}_2)$	7.29		10.2		
(IX) $\text{PSPPh}(\text{NMe}_2)_2$	7.44		12.1		
(X) $\text{PO}(\text{NH}_2)(\text{NMe}_2)_2$ ‡	7.40		10.4		

* For compounds (I)—(VI) spectra were repeated on more concentrated solutions (*ca.* 80%), when shifts were repeatable to 0.01 p.p.m. and coupling constants to 0.5 c./sec. † In cyclohexane. ‡ In CDCl_3 .

derivatives (discussed below) indicate that there is no appreciable change in lone-pair delocalisation from nitrogen. From this it can be inferred that, when a chlorine atom is replaced by a dimethylamino-group, the hybridisation at the nitrogen atom is less affected. By analogy with $^{13}\text{C}-^1\text{H}$ coupling it has been proposed that the hybridisation at phosphorus may be considered in the main to account for changes in $J_{\text{P-H}}$,¹³ as the *s*-character

¹⁶ J. G. Verkade and R. B. King, *Inorg. Chem.*, 1962, **1**, 948.

¹⁷ J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, 1959, p. 184.

¹⁸ J. N. Shoolery, *J. Chem. Phys.*, 1959, **31**, 1427.

¹⁹ N. Muller and D. E. Pritchard, *J. Chem. Phys.*, 1959, **31**, 768.

of a hybrid orbital tends to concentrate in bonds directed towards the most electropositive groups.²⁰ In agreement with this conclusion increasing replacement of dimethylamino groups by chlorine atoms, (III) \rightarrow (I), increases J_{P-H} . There is little difference in the value of J_{P-H} when a dimethylamino-group is replaced by an amino or phenyl group. However, similar arguments would predict a smaller coupling constant for the sulphur derivatives, compared with their oxygen analogues, in contradiction to the experimental results. Comparison of our results with other 1H n.m.r. literature values^{9,12,13,16,21} show that for nine pairs of compounds $J_{P-Y-C-H}$ ($Y = O, N, C$), is greater for thiophosphoryl than for phosphoryl compounds regardless of their chemical shifts.^{9,13,21} The opposite effect reported for two pairs of compounds may be attributed to their unique stereochemistry.¹⁶ For three pairs of compounds^{12,13} the magnitude of J_{P-C-H} is, however, less for those containing the thiophosphoryl than the phosphoryl group.^{12,13} Karabatsos and Orzech²² have pointed out the inadequacy of any correlations between $J_{C-O-C-H}$ and s -character; the same uncertainty besets this even more complex system, where coupling occurs across two hetero-atoms.

The variation of P=O stretching frequency with change in the electronegativities of the groups attached to phosphorus has also been determined (Table 2). This shows that increasingly electronegative substituents increase the P=O stretching frequency.

TABLE 2

Selected infrared absorption frequencies (cm. ⁻¹)				
Compound	$\nu(P=O)$	$\nu(P-N \text{ or } P=S)$	$\nu(C-H)$	
(I) $POCl_2(NMe_2)^*$	1275s	722s	2814w	
(II) $POCl(NMe_2)_2^*$	1241s	758s	2810w	
(III) $PO(NMe_2)_3^\dagger$	1215s	753s	2808w	
(IV) $PSCl_2(NMe_2)$	—	676s, 770s	2807w	
(V) $PSCl(NMe_2)_2$	—	615m, 740m—s, 763s	2800w	
(VI) $PS(NMe_2)_3$	—	714sh, 723s, 742s	2799w	
$POCl_3^*$	1306s	—	—	
$PSCl_3^\ddagger$	—	752s	—	

s = strong; m = medium; w = weak; sh = shoulder.

* R. B. Harvey and J. E. Mayhoad (*Canad. J. Chem.*, 1955, **33**, 1552) report for (I): $\nu(P=O)$, 1268 cm.⁻¹; $\nu(P-N)$, 723 cm.⁻¹; for (II): $\nu(P=O)$, 1241 cm.⁻¹; $\nu(P-N)$, 755 cm.⁻¹; and $POCl_3$; $\nu(P=O)$, 1305 cm.⁻¹. \dagger N. L. Paddock (*Quart. Rev.*, 1964, **18**, 184) reports $\nu(P=O)$, 1212 cm.⁻¹.

\ddagger L. C. Gore (*Discuss. Faraday Soc.*, 1950, **9**, 138) reports $\nu(P=S)$, 752 cm.⁻¹.

Bellamy²³ notes the P=S stretching frequency as a variable band in the region 600—750 cm.⁻¹. More recently Chittenden and Thomas²⁴ have indicated that the same linkage is characterised by bands in the regions 685—862 and 550—730 cm.⁻¹.

Phosphoramidates, as well as phosphazenes containing exocyclic P-N linkages, frequently show a strong absorption band in the region 720—760 cm.⁻¹. Calculations employing Gordy's Rule²⁵ indicate that a P-N stretching frequency would be expected at about 740 cm.⁻¹, probably corresponding to the bands observed for the phosphoramidates in this region. Assignments have recently been made to P=S and P-N stretching frequencies in some cyclic organophosphorus compounds,²⁶ where the bands appear to be well separated.

We observe several bands in the region 600—900 cm.⁻¹, but since no obvious trends are detectable in the P-N stretching frequencies of the phosphoramidates, (I) \rightarrow (III),

²⁰ H. A. Bent, *Canad. J. Chem.*, 1960, **38**, 1235.

²¹ J. B. Stothers and E. Y. Spencer, *Canad. J. Chem.*, 1961, **39**, 1389.

²² G. J. Karabatsos and C. E. Orzech, *J. Amer. Chem. Soc.*, 1964, **86**, 3574.

²³ L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen, London, 1960, p. 321.

²⁴ R. A. Chittenden and L. C. Thomas, *Spectrochim. Acta*, 1964, **20**, 1679.

²⁵ D. E. C. Corbridge and E. J. Lowe, *J.*, 1954, 493.

²⁶ R. S. Edmundson, *Tetrahedron*, 1964, **20**, 2781.

it is difficult to assign with certainty any bands to the P=S group. Only in the case of dimethylphosphoramidothioic dichloride (IV) can the band at 676 cm^{-1} be ascribed with reasonable certainty to a P=S group.

It has been reported that an absorption band in the region 2760—2840 cm^{-1} is due to the symmetric C-H stretching vibration of an NMe group,²⁷ which disappears when the lone pair of electrons on the nitrogen atom of the dimethylamino-group takes part in bond formation. Neither in the mononuclear phosphorus(v) compounds reported here, nor in the dimethylamino-derivatives of the phosphazenes could any variation in intensity of this band with respect to the main absorptions characteristic of the aliphatic carbon-hydrogen bands be detected, indicating no extensive changes in the degree of lone-pair delocalisation, and hence in the state of hybridisation of the nitrogen atom. The band does however show an increase in frequency with increase in the electronegativity of the substituents at the phosphorus atom. Accordingly a lower frequency is observed for the thiophosphoryl than the phosphoryl derivatives.

EXPERIMENTAL

Proton magnetic resonance spectra were obtained at 60 Mc./sec. on a Varian A60 spectrometer. Samples were run in carbon tetrachloride solution (*ca.* 20% w/w) except where otherwise stated. Tetramethylsilane was used as an internal standard. Infrared spectra were obtained from a Unicam S.P. 100 infrared spectrophotometer. These spectra were run on samples dissolved in carbon tetrachloride.

Phenylchlorophosphine oxides and sulphides were obtained from the Victor Chemical Works. Dimethylamino-derivatives were prepared by addition of stoichiometric quantities or excess of dimethylamine to the corresponding chloro-compound. Details are given in Table 3.

TABLE 3

Preparation and analyses of phosphoramidates and phosphorothioic amidates

Com- pound	Preparative method	M. p. or b. p./mm.	Yield (%)	Calc. (%)			Formula	Found (%)		
				C	H	N		C	H	N
(I)	(a)	45°/1	85	14.7	3.7	8.6	C ₂ H ₆ Cl ₂ NOP	15.0	4.4	8.8
(II)	(b)	64/1	91	28.1	7.0	16.4	C ₄ H ₁₂ ClN ₂ OP	28.6	7.1	16.0
(III)	(c)	74/1	90	40.2	10.0	23.4	C ₆ H ₁₈ N ₃ OP	40.4	10.3	23.0
(IV)	(d)	46/0.75	78	13.5	3.4	7.9	C ₂ H ₆ Cl ₂ NPS	13.9	3.5	8.1
(V)	(e)	61/0.5	92	25.8	6.4	15.0	C ₄ H ₁₂ ClN ₂ PS	26.2	6.5	15.1
(VI)	(f)	60/0.1	90	37.0	9.2	21.5	C ₆ H ₁₈ N ₃ PS	37.7	9.5	21.8
(VII)	(g)	168/1	88	68.6	6.5	5.7	C ₁₀ H ₁₇ N ₂ OP	68.0	5.9	5.6
(VIII)	(h)	85	94	56.6	8.0	13.2	C ₁₄ H ₁₆ NOP	56.9	8.4	13.8
(IX)	(i)	47	86	47.3	7.5	12.3	C ₁₀ H ₁₇ N ₂ PS	47.1	7.8	12.2
(X)	(j)	108	80	31.8	9.3	27.8	C ₄ H ₁₄ N ₃ OP	32.3	9.5	27.4

(a) POCl₃ + NHMe₂ at 0°; reflux 12 hr. to remove HCl, vac. dist. (b) (I) + NHMe₂ in CCl₄; removed NH₂Me₂Cl and CCl₄, vac. dist. (c) POCl₃ + excess of NHMe₂ in CCl₄ reflux 1 hr., vac. dist. (d) PSCl₃ + NHMe₂ at 0°; reflux 40 hr., vac. dist. (e) (IV) + NHMe₂ in CCl₄; vac. dist. (f) (V) + excess of NHMe₂ in CCl₄, sealed tube 140°/12 hr., vac. dist. (g) POCl₂Ph + NHMe₂ in Et₂O, reflux 1 hr., sublimed 80°/0.05 mm. (h) POClPh₂ + NHMe₂ in Et₂O, reflux 1 hr., vac. dist. (i) PSCl₂Ph + NHMe₂ in Et₂O, reflux 1 hr., recryst. from pentane. (j) (II) + NH₃ in CHCl₃, remove NH₄Cl and CHCl₃, recryst. from CCl₄.

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