The Phosphorus–Nitrogen Bond. Synthesis, Characterization, and Infrared Studies of Heterocyclic Phosphoryl (Phosphetan) Amides

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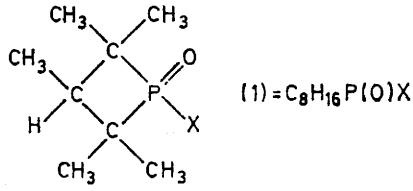
Several new amide derivatives of the heterocyclic 2,2,3,4,4-pentamethylphosphetan 1-oxide (1) have been prepared by heating together the corresponding chloride and amine at elevated temperatures. The products have been characterized by ^1H and ^{13}P n.m.r. spectroscopy and in particular by i.r. spectroscopy over the range 400—4000 cm^{-1}. In one case a mass spectrum is reported in detail. Evidence for hindered rotation about the P–N bond is discussed and interpreted in terms of $p\pi$–$d\pi$ contributions to the bonding.

Of all four-membered heterocyclic phosphorus compounds the *trans*-1-chloro-2,2,3,4,4-pentamethylphosphetan 1-oxide (1; X = Cl) is the easiest to prepare [1,2] and consequently has been intensively studied. The chlorine atom of $C_8H_{16}P(O)Cl$ is fairly resistant to replacement and only a few derivatives such as alkoxyl,[1] methyl,[3] and alkyl thio [4] have been made by this direct method. Substitution of the Cl by amines has only been achieved with benzylamine (overnight refluxing in benzene [5]); yields were low and chromatographic separation of the product necessary. An alternative route to $C_8H_{16}P(O)NHCH_2PH$ involves reduction of $C_8H_{16}P(O)Cl$ to $C_8H_{16}PCl$, with polymethylhydrogensiloxane at 130°, followed by treatment with benzylamine to give $C_8H_{16}PNHCH_2Ph$, and finally H_2O_2 oxidation to the desired product $C_8H_{16}P(O)NHCH_2Ph$.[3]



(1) = $C_8H_{16}P(O)X$

The dimethylamino-derivative, $C_8H_{16}P(O)NMe_3$, has been reported but no preparative details given [6,7] except that in one case [7] it was obtained from $C_8H_{16}PCl$, presumably by the method outlined above.

As part of the study of the phosphorus–nitrogen bond a series of phosphetan amine derivatives have been prepared. The two features of current interest surrounding this particular bond are (i) the possibility of restricted rotation about the P–N bond and (ii) the lack of correlation of P–N vibrational data. Both these effects probably have their origin in the donor N → P $p\pi$–$d\pi$ bonding which can accompany this bond.

EXPERIMENTAL

Instruments.—Phosphorus-31 n.m.r. spectra were recorded on a Bruker HFX 90 spectrometer operating at 36·43 MHz, and referenced to 85% H_3PO_4; the initial signal lock was provided by $CDCl_3$. ^1H N.m.r. spectra were recorded on a Perkin-Elmer R12B spectrometer operating at 60 MHz, and referenced to TMS. Molecular weights were determined on samples dissolved in $CHCl_3$ using a Hitachi–Perkin-Elmer (model 115) osmometer. I.r. spectra were recorded on a Perkin-Elmer 457 spectrometer using CsBr optics. Samples were studied as liquid films, and Nujol or hexachlorobutadiene mulls; chart calibration was checked against the polystyrene band at 1601 cm^{-1}. Mass spectra were recorded on an A.E.I. MS 30 spectrometer operating at 24 eV; samples being introduced as 20—40 w/w % solution in $CHCl_3$ *via* a g.l.c. Carbowax column (210—220 °C) except for the ethanediamino-derivative which was introduced directly as a solid.

Materials.—The amines were standard laboratory reagents suplied by Aldrich [$Me_2N(CH_2)_3NH_2$, $Et_2N(CH_2)_3NH_2$, $Bu^n_2N(CH_2)_3NH_2$], Fisons [Et_3N, Et_2NH, $EtNH_2$, $PhNH_2$, and $PhCH_2NH_2$], B.D.H. [Me_2NH, Pr^nNH_2, Bu^n_2NH, Bu^i_2NH, $C_5H_{10}NH$, $NH_2(CH_2)_2NH_2$], and Hopkins & Williams [Bu^nNH_2]. These amines and all solvents were dried over molecular sieves before use. Only freshly prepared [1] 1-chloro-2,2,3,4,4-pentamethylphosphetan 1-oxide was used and this was recrystallized from petrol (b.p. 60—80 °C).

Preparation of 1-(*NN-Dimethyl*-1,3-*propanediamino*)-2,2,3,4,4-*pentamethylphosphetan* 1-*Oxide and Similar Amides.*—1-Chloro-2,2,3,4,4-pentamethylphosphetan 1-oxide (19·4 g, 0·10 mol) and *NN*-dimethylamino-1,3-propanediamine (20·4 g, 0·20 mol) were heated in refluxing toluene (150 ml) for 3 h under dry, oxygen-free nitrogen. The solution was

[1] J. J. McBride, jun., E. Jungermann, J. V. Killheffer, and R. J. Clutter, *J. Org. Chem.*, 1962, **27**, 1833.
[2] E. Jungermann, J. J. McBride, jun., R. J. Clutter, and A. Maise, *J. Org. Chem.*, 1962, **27**, 606.
[3] D. J. H. Smith and S. Trippett, *Chem. Comm.*, 1969, 855.
[4] J. R. Corfield, R. K. Oram, D. J. H. Smith, and S. Trippett, *J.C.S. Perkin I*, 1972, 713.
[5] W. Hawes and S. Trippett, *J. Chem. Soc.* (*C*), 1969, 1465.
[6] P. Haake and T. Koizumi, *Tetrahedron Letters*, 1970, **55**, 4849.
[7] R. K. Oram and S. Trippett, *Chem. Comm.*, 1972, 554.

filtered to remove the *NN*-dimethyl-1,3-propanediamine dihydrochloride (Found: C, 34·75; H, 8·8; N, 15·65; Cl, 40·5. $C_5H_{16}N_2Cl$ requires C, 34·5; H, 9·0; N, 16·0; Cl, 40·5%). Evaporation of the solvent gave the 1-(*NN-dimethyl*-1,3-*propanediamino*)-2,2,3,4,4-*pentamethylphosphetan* 1-*oxide* in almost quantitative yield. The amber-coloured oil was twice taken up in an equal volume of petrol (b.p. 80—100) and evaporated to give an oil which solidified. Recrystallization from petrol (b.p. 80—100) gave white needle-like crystals, m.p. 102—103 °C.

In a similar experiment, with triethylamine in place of excess amine to take up the evolved HCl, quantitative yields were again obtained.

The preparation of the *NN*-diethyl and *NN*-di-n-butyl-1,3-propanediamine derivatives were carried out in the same manner. The amine dihydrochloride salts were filtered off and the solutions evaporated to give almost quantitative yields of the products as oils which did not solidify.

Attempts to prepare other amine derivatives by this method gave only minute yields of products even after a day's heating under reflux.

Preparation of 1-*Diethylamino*-2,2,3,4,4-*pentamethylphosphetan* 1-*Oxide and Other Amides.*—1-Chloro-2,2,3,4,4-pentamethylphosphetan 1-oxide (9·7 g, 0·05 mol) and diethylamine (7·3 g, 0·1 mol) were dissolved in dry toluene (50 ml) and transferred to a dried thick-walled glass tube which was cooled (CO_2–acetone) and sealed under vacuum. The tube and contents were heated in an electric oven at 215 °C for 5 h. After cooling and opening, diethylamine hydrochloride (5·43 g, 0·05 mol) was removed by filtration and 11·4 g of oil obtained as product after evaporation of the solvent. An equal volume of petrol (b.p. 80—100) was added and removed to give an oil which readily solidified. Recrystallization from petrol (b.p. 80—100) gave white needle-like crystals, m.p. 65—67 °C, of 1-*diethylamino*-2,2,3,4,4-*pentamethylphosphetan* 1-*oxide*.

The preparation of the remaining phosphetan amides listed in Table 1 were carried out in a similar manner. In the case of piperidine, aniline, and benzylamine derivatives triethylamine was used as base to pick up HCl.

Reaction of Phosphetan Anhydride and Diethylamine.—No reaction occurs in ether solution at room temperature after 48 h, or on refluxing. In a Carius tube experiment as described above, the anhydride (4·4 g, 0·014 mol) and diethylamine (2·19 g, 0·045 mol) in toluene (50 ml) gave 2·3 g of the diethylammonium salt of phosphetan acid (0·009 mol), 2·5 g of unreacted anhydride (0·007 mol), plus unidentified product which was not the diethylamino-derivative.

Reaction of Amides with HCl.—A benzene solution of 1-ethylamino-2,2,3,4,4-pentamethylphosphetan 1-oxide (0·84 g, 0·041 mol) was saturated with HCl gas and left at room temperature for 24 h, at the end of which time the insoluble ethylamine hydrochloride was filtered off and the solvent evaporated to give a quantitative yield of the phosphetan chloride (0·81 g, 0·041 mol), confirmed by mixed m.p.

Other amino-derivatives were subjected to the same treatment and all gave quantitative yields; these were the Pr^nNH-, Bu^nNH-, $Bu^n{}_2N$-, $Bu^i{}_2N$-, $Et_2N(CH_2)_3NH$-, $Bu^n{}_2N(CH_2)_3NH$-, and PhNH-derivatives.

[8] J. R. Corfield, N. J. De'ath, and S. Trippett, *Chem. Comm.*, 1970, 1502.

[9] K. Ellis, D. J. H. Smith, and S. Trippett, *J.C.S. Perkin I*, 1972, 1185.

DISCUSSION

Excellent yields of all types of amines (primary, secondary, aliphatic, aromatic, heterocyclic, *etc.*) have been achieved by the simple technique of heating in toluene the phosphetan chloride (1) and excess of amine in a sealed tube at 215 °C. In the case of the *NN*-dialkyl-1,3-propanediamino-compounds the reaction can be performed in refluxing toluene, again producing almost quantitative yields. The corresponding reaction with diethylamine produced only a trace of product even after 24 h. The derivatives prepared, method, yields, m.p., m.w.s., *m/e*, and in some instances elemental analyses are given in Table 1.

That such forcing conditions were required is not totally unexpected in view of the proposed mechanism of nucleophilic substitution.[8] The trigonal-bipyramidal configuration of the intermediate state and the greater electronegativity or apicophilicity of the amine group relative to the resident chloride would explain the slow reaction at lower temperatures. In the case of the *NN*-dialkyl-1,3-propanediamino-derivatives one can conclude that these will substitute at the lower temperature because of their reduced apicophilicity relative to Cl. Steric factors may well be operative with the bulkier amines and the two effects may also work against each other.

Unless precautions are taken rigorously to exclude moisture varying amounts of the phosphetan anhydride, $C_8H_{16}P(O)OP(O)C_8H_{16}$, are produced (unpublished results). Although this ubiquitous compound has so far remained unreported in the phosphetan literature it has remarkable stability with respect to nucleophilic attack, a stability not normally associated with the P–O–P bond. It is stable in cold water.[8] Its reaction at high temperatures with excess of diethylamine did cause a 50% reaction to amine salt of the acid and unidentified product.

With the primary amines there is the possibility of disubstitution at nitrogen but in no case was this observed, steric factors obviously preventing it.

A selection of the amines were treated with HCl [9] and regenerated quantitative yields of the phosphetan chloride.

N.M.R. Spectroscopy.—The ^{31}P n.m.r. spectra (Table 2 all gave a very broad peak due to extensive coupling with all the methyl protons of the phosphetan ring [10] and the protons of the amine fragments. Since the environment of the phosphorus varies only as a secondary effect in these derivatives, and considering their general similarity anyway, it is not surprising that all the shifts fall within a narrow range. In order of shift the sequence is $C_5H_{10}N$-(2) > $-NH(CH_2)_2NH$-(9) > $PhCH_2NH$-(10) = $Bu^n{}_2N$-(1) > Et_2N-(8) > $Bu^i{}_2N$-(4) > Pr^nNH-(7) > $Me_2N(CH_2)_3NH$- > $Et_2N(CH_2)_3NH$- > $Bu^n{}_2N(CH_2)_3NH$- > EtNH-(6) > Me_2N-(5) > PhNH-(11). The number in parentheses shows the order of base strengths as measured by the pK_1 values of the amines.[11] There is no relationship between the two properties.

[10] S. E. Cremer and B. C. Trivedi, *J. Amer. Chem. Soc.*, 1969, **91**, 7200.

[11] 'Handbook of Tables for Organic Compound Identification,' 3rd edn., p. 436, Chemical Rubber Co., Cleveland, Ohio, 1967.

The p.m.r. spectra were invariably complex in the δ region 0·80—2·00 p.p.m. In no case was either the primary amide proton, or the single proton attached to the phosphetan ring, observed. The most interesting spectrum was that of the dimethylamino-derivative which showed a pair of doublets centred at 2·63 and 2·71 atmospheric moisture, *etc.*, shows the pair of doublets illustrated in the Figure (a). On exposure to air these degenerate to a single pair [Figure (b)]. A similar effect was noted by Trippett for the CH_2 protons of $C_8H_{16}P(O)NCH_2Ph$ [5] and he attributed the loss of structure to protonation.

TABLE 1

Amino-derivatives of 2,2,3,4,4-pentamethylphosphetan 1-oxide

$C_8H_{16}P(O)X$ X =	Method [a]	Yield (%)	M.p. (°C)	M Calc.	M Obs.[b]	*m/e*	Intensity [c]	Analyses [d] (%) C	H	N	P
–NHEt	ST	100	111—112	203	203	203	24	58·85 (59·1)	11·05 (10·85)	7·0 (6·80)	
–$NHPr^n$	ST	98	112—113	217	216	217	20				
–$NHBu^n$	ST	94	96—98	231	230	231	18	60·10 (62·25)	10·95 (11·25)		
$-NMe_2$	ST	98	94—95	203	203	203	12	59·15 (59·1)	11·15 (10·85)	6·70 (6·90)	
$-NEt_2$	ST	97	65—67	231	231	231	12	61·95 (62·20)	11·55 (11·25)	6·00 (6·05)	13·45 (13·40)
$-NBu^n_2$	ST	97	140—141	287	288	287	5				
$-NBu^i_2$	ST	96	162—163	287	287	287	4				
$-NH(CH_2)_3NMe_2$	RT	96	102—103	260	260	260	13	60·00 (60·00)	10·60 (10·30)	10·75 (10·80)	12·15 (12·10)
$-NH(CH_2)_3NEt_2$	ST RT	98 95	Oil	288	284	288	2				
$-NH(CH_2)_3NBu^n_2$	ST RT	98 100	Oil	344	339	344	2				
$-NHCH_2CH_2NH-$	ST	91	280 [e]	376	374	376	28	57·05 (57·45)	10·30 (10·10)	7·55 (7·45)	
$-NC_5H_{10}$	ST	84	69—71	243	243	243	16	64·15 (63·95)	11·0 (10·65)	5·55 (5·75)	
–NHPh	ST	97	Oil	251	251	251	47	66·25 (66·92)	8·95 (8·35)	5·65 (5·55)	
$-NHCH_2Ph$	ST	94	158—159 [f]	265	267	265	4				

[a] ST = Sealed tube; RT = refluxing toluene. [b] ±2%. [c] % Base peak. [d] Calculated values in parenthesis. [e] Decomposes. [f] Lit., 159—160, ref. 5.

TABLE 2

N.m.r. spectra of the amino-derivatives of 2,2,3,4,4- pentamethylphosphetan 1-oxide

$C_8H_{16}P(O)X$ X =	^{31}P n.m.r. δ(p.p.m.) [a]	^1H N.m.r. δ(p.p.m.) [b] [integral, structure,[c] coupling constant,[d] *J*/Hz] [e]
–NHEt	53·93	0·89 [3H, d, 8]; 1·19 [6H, d, 18); 1·24 [6H, d, 18]; 1·29 [3H, b, 5]; 3·21 [2H, qi, 7];
–$NHPr^n$	55·71	0·97 [3H, d, 8]; 1·21 [12H, d, 17]; 2·98 [2H, q, 7]; CH_2CH_3 of n-propyl not clearly distinguished
–$NHBu^n$	56·05	0·90 [3H, d, 7]; 1·18 [6H, d, 17]; 1·24 [6H, d, 17]; 2·98 [2H, q, 7]; $CH_2CH_2CH_3$ of n-butyl not clearly distinguished
$-NMe_2$	53·42	0·89 [3H, m, –]; 1·50 [6H, d, 17]; 1·58 [6H, d, 17]; 2·63 [3H, d, 11]; 2·71 [3H, d, 11]; see text
$-NEt_2$	56·23	0·90 [3H, d, 7]; 1·17 [6H, t, 7]; 1·20 [6H, d, 18]; 1·25 [6H, d, 18]; 3·08 [4H, t, 7];
$-NBu^n_2$	56·33	0·86 [3H, d, 7]; 1·25 [12H, d, 18]; 2·95 [4H, q, 8];
$-NBu^i_2$	55·77	0·80—2·00 region too complex for identification; 2·80 [4H, q, 8]
$-NH(CH_2)_3NMe_2$	54·85	0·86 [3H, d, 8]; 1·17 [6H, d, 18]; 1·22 [6H, d, 18]; 1·75 [2H, q, 6]; 2·27 [6H, s]; 2·46 [2H, q, 6]; 3·12 [2H, m, –]
$-HN(CH_2)_2NEt_2$	54·83	0·86 [3H, d, 7]; 1·04 [6H, s]; 3·16 [2H, qi, 6];
$-NH(CH_2)_3NBu^n_2$	54·27	1·18 [6H, d, 18]; 1·23 [6H, d, 17]; 3·14 [2H, qi, 6];
$-NH(CH_2)_2NH-$	57·33	0·84 [3H, d, 7]; 1·23 [12H, d, 18]; 3·16 [4H, m, –];
$-NC_5H_{10}$	57·56	0·87 [3H, d, 7]; 1·23 [6H, d, 17]; 1·27 [6H, d, 17]; 1·58 [6H, m, –]; 3·06 [4H, q, 4]
–NHPh	51·86	0·92 [3H, m, –]; 1·30 [6H, d, 18]; 1·36 [6H, d, 18]; 7·15 [5H, m, –];
$-NHCH_2Ph$	56·33	0·90 [3H, m, –]; 1·18 [6H, d, 18]; 1·28 [6H, d, 18]; 4·22 [2H, t, 7]; 7·38 [5H, s]

[a] 85% H_3PO_4. [b] TMS. [c] s, Singlet; d, doublet; t, triplet; q, quartet; qi, quintet; m, multiplet. [d] To phosphorus. [e] Some spectra are too complex for all their peaks to be assigned or reported.

which are the methyl protons of the nitrogen; *J*(PNCH) 10·8 Hz. This distinguishing of the two nitrogen methyl groups is strong evidence for restricted rotation about the P–N bond.

A similar situation can occur for the C–N bond in amides. There is hindered rotation about this bond in *NN*-dimethylformamide [12] and at 35 °C two distinct peaks are observed for the two methyls.

Freshly prepared $C_8H_{16}P(O)NMe_2$, kept free from

If donor $p\pi$–$d\pi$ N–P bonding, using the non-bonding pair of electrons of the nitrogen, were to supplement the *sigma* bond this could well be responsible for restricted rotation as observed. Protonation of the nitrogen lone pair would destroy the π-system and rotation about the P–N bond would then cause equivalence of the two methyl groups. Other P–N systems have recently been described in which restricted rotation about this

[12] F. A. Bovey, *Chem. Eng. News*, 1965, **43**, 98.

TABLE 3

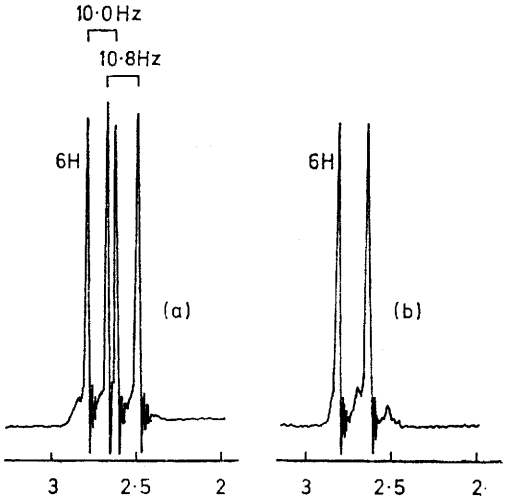
The i.r. spectra (400—4000 cm^{-1}) of the amino-derivatives of 2,2,3,4,4-pentamethylphosphetan 1-oxide, $C_8H_{16}P(O)X$

NHEt	NHPr^n	NHBu^n	NMe_2	NEt_2	NBu^n_2	$NBui_2$	$NH(CH_2)_3$-NMe_2	$NH(CH_2)_3$-NEt_2	$NH(CH_2)_3$-NBu^n_2	$NH(CH_2)_2$-NH	NC_5H_{10} †	NHPh	$NHCH_2Ph$	
			395sh											
398w	398w	398w	403w	400vw	408w	400w	395w	398w	395w	395w	400w	395w	400w	Phosphetan
									410w			410w		
			415w	418w	419w	418m	418w	418sh	418sh		420w			$\delta(NC_2)$
428w	425w	430w	430w	430m	430s	432s	428sh	425w	432w	424m	432m	430m		
			440w							434m			438m	
	455vw	450vw					450vw	460w	460w		445m			
		472w			470m	470m	470w		470w		490w	473m	472vw	
					498w							498sh		
			504m	505w	505w	500sh	505sh	505sh	500w	508m	500m	503m	508m	}
518m	515m	518m	518s	524s	523s	520s	518s	520ms	518m		515m			phosphetan
										528m		520s	524m	}
522sh	525sh	525sh	530s	530sh	530sh	525s	533m	530sh	530sh		525s			
											536m			
556w	550w	557w	557w	555w	555m	560m	555w	555w	553w	555w	550sh	555vw	555vw	phosphetan
			600w		589w	598m								
											615sh			
630w	625w	630w	630w	630m	627m	625m	622w,sh	630sh	625sh	630m	603m	630m	629m	phosphetan
658m	658m	665m	660s	660s	670s	670s	658s	659s	660s	655m	665s	670s	659m	phosphetan
							687m	692m	690m			693s	694s	
				702s					710w		708s			
		732m	724vs					726s	727s		720s	725m	727s	
750w	745m	750sh	756s	749m	750s	755ms	752s	750m	750m	748w	755s	750vs	750sh	phosphetan
776s	760sh	760sh		760sh				760sh	760sh	769m				δ(N–H)?
		785w		775m										see text
			800vw	790ms						793w	805w	790w		
											815w	820w		
830m	835m						828vs	830w	825w,br		832ms		830sh	δ(N–H)?
														see text
		855w	850w				843w			845m			845m	
										862m	854ms			
	880w	890m	890w	890vw	895s		889m,br	890m,br	895s	888w	890w	890sh	895w	
	895m			910m		900s	910vw	910sh	910sh	915w		910vs	910sh	
927s	925m	925s	930sh	930vs	932vs,br	930s,br	928s	925m	927s	925s	935sh	925sh	923m	phosphetan
947s	945w	950m	952vs	940sh	957vs	950m	940m	940w,br	940sh	940m	954vs	941m	940w	} amine
							950m				955sh			} carbon
		960sh					965sh			968sh				} framework
987m	987sh	980m	979s	985w			988m	985w	984w	982m	976w	993m	980w,br	ν(C–C)
			985sh				1005sh							
1015w	1010w	1018w	1018m	1015s	1020m	1017m	1018m	1015w	1015w	1015w	1020w	1015sh	1020m	}
	1025w	1035m					1038s	1028w	1026sh		1035w	1028m		}
1043w	1047m	1050w	1050m	1055w	1048m	1045m	1043sh	1045m	1046m	1044w	1055vs	1048m	1043w	$\rho(CH_3)$
							1060s							
1068s	1070w	1070m	1070m	1069w	1075m	1075m	1072m	1070sh	1080sh	1070w	1075w	1070m	1068m	}
	1090m	1095m		1093w			1098vs	1095vs	1100vs	1090m	1096m		1095m	} ν(CN)
	1100m		1103w			1103w	1105sh						1105m	} see text
1115s	1125s	1125m						1120m			1118w			
			1148sh		1150sh			1150sh	1150sh	1145s	1140m			
1159s	1155vs	1160vs	1156vs	1158s	1160s	1152sh	1150vs	1160vs	1160s	1160s	1158s	1158s	1150s	ν(PN)
			1180s	1175sh		1170s	1182s	1182vs	1180s				1177m	
				1190sh								1185s		
1195sh	1178s	1180sh	1195s	1205vs	1210vs	1210vs	1192ssh	1190ssh	1205sh	1200ssh	1194vs	1210s	1193m	} ν(P=O)
		1205sh									1210sh			
1230s	1236s	1236s	1236s	1230s	1235sh	1235sh	1235m	1233s	1234s	1235s	1235s	1230s	1236s	phosphetan
		1255sh			1255vs	1255vs					1255w			ν_{as}(CPC)
			1263m	1282w	1265vs	1265vs	1265m	1260m	1255m		1273m	1260s		$\nu(NC_2)$
1278m												1278s		ν(CN) of PhNH
	1290vw	1295vw	1286m					1288m	1295w	1292m			1295w	
	1310vw						1302m			1310w	1312m			
1340w	1330vw			1335w						1330w	1332m		1355m	}
1365m	1360sh	1367m	1362m	1360sh	1365m	1362m	1367m	1360m	1358sh	1362m	1355sh	1365m	1367m	}
1375m	1375m	1378m	1375m	1372s	1377m	1379m	1380m	1375m	1378s	1374m	1370s	1375m	1377m	} $\delta_s(CH_3)$
1385m	1385m	1390m	1385m	1382sh	1387m	1385m	1388m	1382sh	1384sh	1382m	1382sh	1387ms	1389m	}
												1395m		ν(C–C)
										1428m	1435sh			phenyl
1450sh	1450sh	1450sh		1450sh	1450s	1450sh				1445sh	1445sh	1450sh	1450vs	}
1460s	1460s	1465s	1455vs,br	1457s	1460s	1460s	1455bs,br	1460vs,br	1460vs,br	1455vs	1460s	1460s	1460sh	} $\delta_{as}(CH_3)$
				1470sh		1470sh				1468sh	1465sh			}
												1491s	1490m	
						1585m						1598vs		
							1640w,br			1620w		1620m		
			2480w			2420w								
						2530sh								
			2590w			2560w								
		2670w	2665w							2660w				
		2710w					2720m	2710m	2720w	2715vw				
						2740m	2760s	2790m	2790m					
			2800m				2810s							
2850s	2860s	2860s	2860sh	2860s	2855s	2860s	2860s	2855s	2860vs	2852s	2850s	2855s	2860s	}
				2895sh	2890sh	2890sh				2880sh				} ν_{as} and ν_s
2920sh	2920sh	2930sh	2920vs	2920s	2920sh	2920sh	2920sh	2920sh	2920sh	2935vs	2930vs	2920sh	2920sh	} (CH_3)
2960vs	2950vs	2950vs	2970vs	2970vs	2960vs	2960vs	2950vs	2980vs	2950vs	2960vs	2960vs	2960vs	2960vs	}
												3030w	3020w	
												3070w	3060w	
													3080w	
3195vs,br	3180vs,br	3200vs,br					3190s,br	3190s,br	3195s,br	3170s		3200m,br	3190vs,br	ν(N–H)
										3220sh				
										3250vs				

† Piperidino.

bond is reported and the presence of a $p\pi$–$d\pi$ system inferred.[13]

Infrared Spectroscopy.—It is generally recognized that absorption frequencies of the P–C and P–N bonds do not fall within well defined regions of the infrared spectrum.[14–16] Nevertheless a ring such as the phosphetan ring might be expected to have certain characteristic vibrations associated with the C_3P ring or the CPC fragment. So far no detailed i.r. spectra have been reported or discussed. The study of a series of very similar compounds such as the amides should be capable of bringing such characteristic modes to light as well as



^{1}H N.m.r. spectra of Me_2N protons of $C_8H_{16}P(O)NMe_2$ (a) initially; (b) on standing in contact with air [δ/p.p.m. Me_4Si]. Both sets of peaks represent 6H relative to the remainder of the spectrum in each case, *i.e.* the total intensity of the (a) quartet is equal to that of the doublet of (b) on a comparative basis

offering the chance of assigning the elusive P–N stretching vibration. The spectra of Table 3 can be discussed most readily in terms of the following groups.

The Methyl Vibrations.—These, principally of the phosphetan ring, occur in the expected regions: 2850—2970, ν_s and ν_{as} (CH_3); 1450—1470, δ_{as} (CH_3); 1360—1390 δ_s (CH_3); and 1015—1075 cm^{-1} ρ(CH_3). The rocking and symmetrical bending vibrations often occur as a triplet of peaks of similar intensity.

The N–H *Vibrations.*—The stretching modes are found as strong, broad bands at 3180—3200 cm^{-1} in the nine derivatives with this group. The broadness indicates H-bonding. The *NN'*-diaminoethane compound has two strong bands in this region, presumably due to in- and out-of-phase combinations.

The N–H bending vibrations are expected[15] at 1400 ± 30 and *ca.* 750 cm^{-1}. Like Chittenden and Thomas[16] we have been unable to identify the higher band but the 750 cm^{-1} band may be seen as a shoulder to a phosphetan framework mode with this frequency. However, not all the nine show this band and its presence in the diethylamino-derivative also weakens the assignment. An alternative choice of bands is at 830 cm^{-1} but again conclusive proof is lacking.

The Phosphoryl Vibration.—The ν(P=O) mode has been extensively studied since it was shown possible to calculate its position in the spectrum by the use of empirical formulae (1) such as that of Thomas and Chittenden.[17] With $\pi = 4{\cdot}2$ for the phosphetan ring ν(P=O)

$$\nu(P{=}O) = 930 + 40\,\Sigma\,\pi \text{ cm}^{-1} \qquad (1)$$

are predicted at 1178 and 1186 cm^{-1} for primary and secondary amides. Inspection of Table 3 shows a range of intense vibrations in the region 1178—1210 cm^{-1} which are consequently assigned to ν(P=O).

In some spectra the phosphoryl band occurs as a shoulder to another intense series of peaks at 1150—1160 cm^{-1}. There is evidence of other shoulders which may be due to the ' phosphoryl doublet ' effect variously attributed to conformers[18,19] or Fermi resonances.[20] It seems likely that if the 1150—1160 cm^{-1} peaks are due to ν(PN), as will be argued, then extensive coupling between these two vibrations is occurring.

The Carbon–Nitrogen Vibrations.—This mode is expected[21] in the range 1020—1220 cm^{-1} which can be narrowed to 1076—1144 cm^{-1} for phosphoryl amides.[16] For phosphoryl anilide derivatives a band at 1266—1316 is assigned to ν(C–N)[21] and a peak at 1278 cm^{-1} in $C_8H_{16}P(O)NHPh$ is so allotted. For alkyl amides ν(C–N) is not easily assigned but inspection of all the spectra show bands in the region 1076—1144 cm^{-1}. The stretching and bending vibrations of NC_2 should be present in eight of the derivatives and are recognized as falling at 1263—1282 and 315—420 cm^{-1} respectively.

Phosphetan Framework Vibrations.—In the main these should be unaffected by changes at nitrogen and should therefore fall within a narrow range in all these derivatives. If any of the phosphetan framework modes are sensitive to changes at nitrogen then presumably these involve the phosphorus atom. Furthermore they should also be observed in other phosphetan derivatives of the type $C_8H_{16}P(O)X$ and in this respect derivatives where X is –OR (R = Me, Et, Pr, *etc.*), –Cl and –OH have been consulted.[22]

Using these criteria the following bands are chosen as originating in vibrations of the phosphetan framework: 1230—1236, 925—935, 745—756, 655—670, 625—630, 550—560, 515—530 (doublet with shoulders), and 398—408 cm^{-1}. Of these the first is found at 1248—1253 cm^{-1} in the alkoxides, 1257 and 1242 cm^{-1} respectively in

[13] A. Hung and J. W. Gilje, *J.C.S. Chem. Comm.*, 1972, 662 and references therein.
[14] F. F. Bentley, D. L. Smithson, and A. L. Rozek, ' Infrared Spectra and Characteristic Frequencies 700—300 cm^{-1},' Interscience, New York, 1968.
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[21] N. B. Colthup, *J. Opt. Soc. Amer.*, 1950, **40**, 397.
[22] Unpublished spectra of the authors.

the chloride and acid phosphetan derivatives. This band is the most sensitive to changes at phosphorus and since all the remaining phosphetan peaks are remarkably unaffected by changes at phosphorus.

TABLE 4

Mass spectrum of 1-piperidino-2,2,3,4,4-pentamethyl phosphetan 1-oxide

m/e	% [a]	Fragment [b]
245	2	$M + 2$
244	8	$M + 1$
243	16	M, $C_8H_{16}P(O)NC_5H_{10}^+$
242	2	$M - 1$
231	1	$F + 2$
230	1	$F + 1$
229	2	F, $C_8H_{16}P(O)NC_4H_8^+$
228	3	$F - 1$
217	1	$F + 2$
216	2	$F + 1$
215	1	F, $C_8H_{16}P(O)NC_3H_6^+$
214	1	$F - 1$
203	1	$F + 2$
202	1	$F + 1$
201	2	F, $C_8H_{15}P(O)NC_2H_4^+$
200	2	$F - 1$
189	1	$F + 2$
188	2	$F + 1$
187	1	F, $C_8H_{16}P(O)NCH_2^+$
186	1	$F - 1$
175	7	$F + 2$
174	3	$F + 1$
173	6	F, $C_8H_{16}P(O)N^+$
172	2	$F - 1$
160	2	$F + 1$
159	4	F, $C_8H_{16}PO^+$
158	1	$F - 1$
144	2	$F + 1$
143	2	F, $C_8H_{16}P^+$
142	3	$F - 1$
133	10	$F + 2$
132	79	$F + 1$
131	8	F, $P(O)NC_5H_{10}^+$
130	56	$F - 1$
129	1	$F - 2$
128	16	$F - 3$
127	10	$F - 4$
126	71	$F - 5$
118	3	
117	1	$F + 2$
116	9	$F + 1$
115	56	F, $PNC_5H_{10}^+$
114	2	$F - 1$
113	9	$F - 2$ or $C_8H_{17}^+$
112	100	$C_8H_{16}^+$
111	2	$C_8H_{15}^+$
98	10	$F + 1$
97	100	F, $C_7H_{13}^+$
85	4	$F + 1$
84	34	F, $NC_5H_{10}^+$

[a] Of base peak. [b] F = fragment, $+2$ = 2H and/or H + ^{13}C, *etc.*

is consequently assigned to ν_{as}(CPC). The corresponding ν_s(CPC) cannot with certainty be identified by this method

[23] I. N. Zhumurova, A. A. Kisilenko, and A. A. Kirsanov, *J. Gen. Chem. U.S.S.R.*, 1962, **32**, 2544.

The Phosphorus–Nitrogen Vibration.—There are two claimants to this, a series of bands at 940—957 and another at 1150—1160 cm^{-1}. The former varies greatly in intensity from very weak to very strong and is sometimes a shoulder on the phosphetan band at *ca.* 930 cm^{-1}. This ' series ' of bands is more likely to be amide framework modes. The latter series is consistently strong to very strong in all derivatives and yet it lies beyond the upper limit for ν(PN) of 873—1053 cm^{-1} found by Chittenden and Thomas.[16] Why is it so high? A likely explanation is again $p\pi$–$d\pi$ contributions to the N–P bonding.

The location of ν(P=N) in those compounds with this bond, *e.g.* $Ph_3P{=}NR$, is put at 1330—1370 cm^{-1}.[16,23] In the cyclic phosphonitriles, in which a delocalized $p\pi$–$d\pi$ bonding is present (as shown by equality of ring bond lengths) the ν(PN) vibration is at 1175—1438 cm^{-1}, its position dependent upon ring size and the electronegativity of the groups attached to the P atoms.[24,25] On a comparable basis with $Ph_3P{=}NR$ the cyclic phenyl phosphonitriles have ν(PN) at 1190 $(Ph_2PN)_3$ and 1213 cm^{-1} $(Ph_2PN)_4$.

For single P–N bonds there is no correlatable range of values of ν(P–N) suggesting that some factor other than electronegative consideration is operative. The cause may well lie with $p\pi$–$d\pi$ contributions, the larger these are the stronger the bond, the higher the wavenumber. A range of 1150—1160 cm^{-1} as assigned to the P–N bond in the phosphetan amides suggests a significant π contribution, which in turn would lead to a higher rotational energy barrier.

Mass Spectroscopy.—A mass spectrum was taken for every derivative and in all cases the molecular ion was observed (Table 1). Most spectra were extremely complex especially below *m/e* 112 ($C_8H_{16}^+$). In most spectra no single peak had a relative intensity of more than 5%. The complexity arises partly as a result of a significant percentage of molecules incorporating a ^{13}C atom.

In Table 4 the spectrum of the piperidino-derivative is analysed, this compound giving the least complicated spectrum. [Even so below 112 there is a peak for every mass unit although in the range 55—111 only the 4 reported in Table 4 are prominent.] In this, as in other spectra, the fragmentation pattern cannot be accounted for by loss of methyl groups from the phosphetan ring. In the piperidino-derivative loss of such CH_3 would have produced *m/e* values at 228, 213, 198, 183, and 168. Instead the spectrum can be accounted for by loss of CH_2 units from the amine.

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[25] J. Emsley, *J. Chem. Soc.* (*A*), 1970, 109.