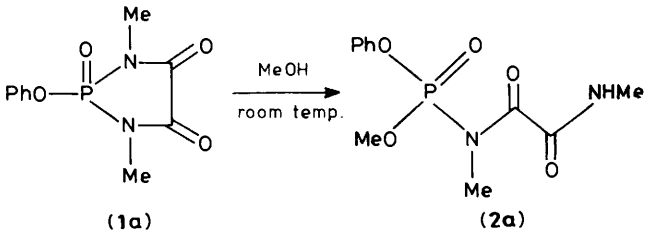
Phosphoric Carboxylic Imides. Part 6.† Structure and Reactivity of 1,3,2-Diazaphospholidine-4,5-diones; Crystal Structure‡ of 1,3-Dimethyl-2-methylamino-1,3,2-diazaphospholidine-2,4,5-trione

Alan T. Hutton, Tomasz A. Modro,* Margaret L. Niven, and Sonia Scaillet
School of Chemical Sciences, University of Cape Town, Rondebosch 7700, South Africa

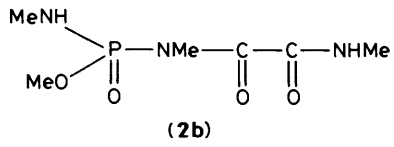
1,3-Dimethyl-2-methylamino-1,3,2-diazaphospholidine-2,4,5-trione (**1b**) has been synthesized, and its solvolytic behaviour and *X*-ray crystal structure determined. Methanolysis of (**1b**) gives products of the cleavage of *both* imide P–N bonds, indicating that the ring opening in (**1b**) is much slower than the second P–N cleavage in the ring-opened intermediate. The low reactivity of (**1b**) is correlated with the small size (92.3°) of the endocyclic N–P–N angle, which suggests that not much energy is released upon the formation of the P^V trigonal bipyramidal adduct. The molecular structure of (**1b**) reveals a high degree of coplanarity of the phospholidine ring with both imide *N*-methyl groups and both carbonyl oxygen atoms. The geometry indicates that the endocyclic nitrogen atoms in (**1b**) are involved in the resonance interactions not only with the adjacent carbonyl groups, but also with the phosphoryl centre.

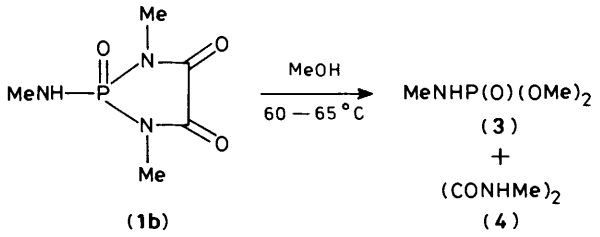
1,3-Dimethyl-2-phenoxy-1,3,2-diazaphospholidine-2,4,5-trione (**1a**) has been found to react with *p*-anisidine or ammonia exclusively at the phosphorus atom. In the reaction with *p*-anisidine both P–O bond cleavage (displacement of phenol) and ring P–N bond cleavage products were obtained; this is interpreted in terms of pseudorotation of the initially formed P^V intermediate. Ammonia reacts with (**1a**) giving exclusively the ring-retained, P–OPh bond cleavage products. Our aminolysis results for (**1a**) contrast with those reported in the literature.

In his studies on the nucleophilic cleavage of the 1,3,2-diazaphospholidine system, Mulliez[1] found that 2-phenoxy, 2-ethoxy, and 2-phenyl derivatives undergo methanolysis with cleavage of only one P–N bond, yielding ring-opened products which were relatively stable towards further solvolysis. This behaviour is illustrated in Scheme 1, which shows the methanolysis of 1,3-dimethyl-2-phenoxy-1,3,2-diazaphospholidine-2,4,5-trione (**1a**). The much greater reactivity of the P–N bond in (**1a**) than in (**2a**) was taken as evidence for the addition–elimination mechanism of solvolysis, since in such a case (**1a**) would experience the usual rate-accelerating effect upon the formation of the P^V intermediate with trigonal bipyramidal structure. The reluctance of the product (**2a**) to undergo further methanolysis is not surprising; we have demonstrated[2] that at 25 °C P–N bond cleavage by methanol in the structurally related dimethyl *N*-methyl-*N*-acetylphosphoramidate, $(MeO)_2P(O)NMeAc$, is slow ($t_{\frac{1}{2}}$ *ca.* 100 h).



Scheme 1.





Scheme 2.

We report here that a change in the exocyclic *P*-substituent in a 1,3,2-diazaphospholidine can dramatically affect the relative reactivities of the two initially endocylic P–N bonds. We have synthesized 1,3-dimethyl-2-methylamino-1,3,2-diazaphospholidine-2,4,5-trione (**1b**) and found it to be indefinitely stable in methanol at room temperature.§ The solvolysis of (**1b**) could be achieved at elevated temperature, but it invariably resulted in cleavage of *both* imide P–N bonds (Scheme 2).

Under no circumstances were we able to detect the product of cleavage of the first P–N bond in (**1b**), *i.e.* the ring-opened carboxylic phosphoric imide (**2b**). This proves that solvolysis of (**2b**) is much faster than the initial solvolytic cleavage of the cyclic substrate (**1b**). The reasons for this difference in the solvolytic reactivity of the imide P–N bond in (**2b**) and the endocyclic bond in (**1b**) could be manifold. The phosphorus atom in (**1b**), substituted by three nitrogen atoms, is certainly less electrophilic than the phosphorus atom in the monoester derivative (**2b**). We believe, however, that the observed low reactivity of (**1b**) stems at least partly from its molecular geometry. According to a generally accepted theory[3] which explains the abnormally high reactivity of phosphoric derivatives in which the phosphorus atom is constrained in a five-

† Part 5, T. F. Hendrickse and T. A. Modro, *Phosphorus Sulfur*, 1984, **20**, 247.

‡ *Supplementary data available* (No. SUP 56385, 3 pp.): H-atom coordinates, thermal parameters. For details of Supplementary Publications see Instructions for Authors, *J. Chem. Soc., Perkin Trans. 2*, Issue No. 1, 1986.

§ The ^1H n.m.r. spectrum of (**1b**) incubated in methanol at 25 °C did not show any noticeable change after 1 430 h.

Table 1. Bond lengths (Å) and bond angles (°), with e.s.d.s in parentheses

	Compound		
Bond	(**1b**)	(**4a**)[a]	(**5**)[b]
P=O	1.466(4)		1.461(4)
P–N(amide)	1.601(10)		
(amide)N–Me	1.461(15)		
P–N(imide)	1.673(10)		1.667(5)
(imide)N–Me	1.461(14)	1.449(2)	
N–C(O)	1.371(12)	1.323(2)	1.393(7)
C=O	1.218(14)	1.227(2)	1.219(6)
C(O)–C(O)	1.495(16)	1.544(3)	
Angle			
P–N–Me(amide)	123.1(6)		
N–P=O(amide)	112.5(4)		
N–P–N(exo)	109.5(5)		
N–P=O(imide)	115.7(14)		107.5(2)
N–P–N(endo)	92.3(1)		
P–N–Me(imide)	123.1(8)		
Me–N–C(O)	122.6(8)	122.5(2)	
N–C=O	125.7(8)	125.4(1)	120.0(5)
O=C–C(O)	124.7(11)	121.4(2)	
(O)C–C(O)–N	109.6(10)	113.3(2)	117.1(5) [Ph–C(O)–N]
(O)C–N–P	114.2(9)		124.7(4)

[a] Ref. 7. [b] Ref. 8.

membered ring, significant release of strain is achieved when the two endocyclic bonds of a substrate attain an apical-equatorial configuration in the intermediate bipyramidal structure. In a typical case of the conversion of a five-membered cyclic phosphate into the trigonal bipyramidal intermediate, the endocyclic O–P–O angle is reduced from *ca.* 99 to *ca.* 90°, with release of *ca.* 3—6 kcal mol^{-1}.[4] This stereoelectronic effect on the rate of nucleophilic cleavage has been found to operate also in the base[5]- and acid[6]-catalysed hydrolysis of 1,3,2-oxazaphospholidines. We decided to determine the molecular structure of the substrate (**1b**) in order to obtain more information about the geometry changes which could be involved in the association step of the solvolysis. In addition, since no molecular structures for 1,3,2-diazaphospholidine-2,4,5-triones have been reported, we hoped that the *X*-ray diffraction study of (**1b**) would provide insight into the molecular parameters characteristic of this system. The molecular structure of (**1b**) could then be compared with that of *N*,*N*′-dimethyloxamide (**4**) itself,[7] to see the effect of ring closure on the oxamide skeleton. It could also be related to the recently determined[8] structure of the acyclic phosphoric carboxylic imide, dimethyl *N*-benzoylphosphoramidate (**5**). The molecular structure of (**1b**) is shown in Figure 1, and the bond lengths and angles [together with the relevant data for (**4**) and (**5**)] are given in Table 1.

The structures of compounds (**1b**), (**5**), and (**4**) will be discussed in the next section. However, the most important feature of the molecular structure of the cyclic substrate (**1b**) relevant to its solvolytic behaviour is the very small endocyclic N–P–N angle (92.3 ± 0.1°). Although structural data on cyclic P^{IV} derivatives are scarce, the N–P–N angle in (**1b**) corresponds closely to the endocyclic N–P–N angle (91.8°) found in 2-dimethylamino-1,3-diphenyl-2-phenylimino-1,3,2-diazaphospholidine.[9] We believe that the small N–P–N angle in (**1b**), being close to 90°, is responsible for the absence of the usual energy release upon formation of a trigonal bipyramidal intermediate (**6b**) (Scheme 3), and hence the absence of reactivity enhancement in nucleophilic cleavage.*

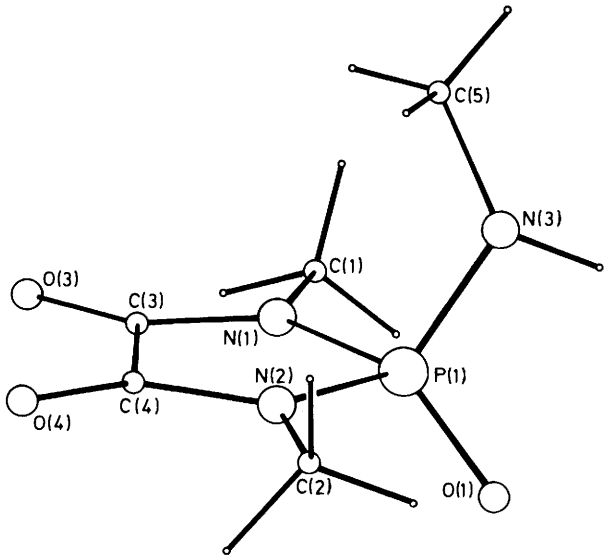
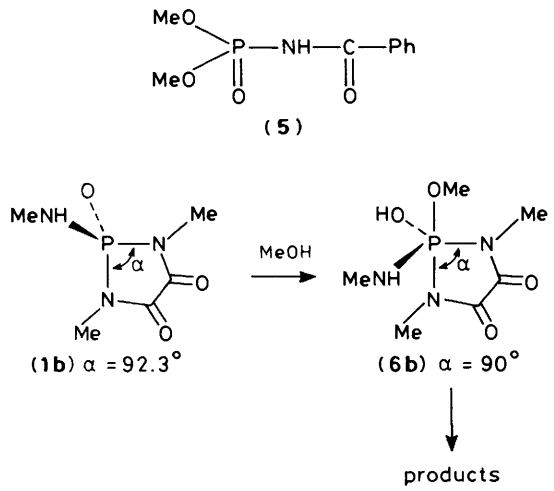


Figure 1. Perspective view (and atom numbering) of the molecule of 1,3-dimethyl-2-methylamino-1,3,2-diazaphospholidine-2,4,5-trione (**1b**)

The imide (endocyclic) P–N bonds in (**1b**) are rather longer, and the amide (exocyclic) P–N bond is rather shorter than the P(O)–N distance of 1.61—1.67 Å observed for most phosphoric amides. This is certainly the result of the electronic effects of both carbonyl groups, which modify the order of the P–N bonds involved. However, the bond order of the phosphoryl centre

* According to this interpretation, the N–P–N angle in (**1a**) should be significantly larger than that in (**1b**). We have tried to determine the molecular structure of (**1a**), but unfortunately, because of the highly hygroscopic nature of this compound, all attempts to grow suitable crystals have failed; the only crystalline material isolated proved to be the hydrolysis product (**4**).



Scheme 3.

determines the magnitude of the repulsions involving each pair of bonding orbitals, and is responsible for the distortion of the bond angles of phosphorus from an ideal tetrahedral geometry.[10] In consequence, the two short, high-order bonds in (**1b**) (the phosphoryl and the amide bonds) cause narrowing of the endocyclic N–P–N angle which involves two long, low-order imide bonds.

During his investigation of the methanolysis of (**1a**) (Scheme 1), Mulliez[1] did not observe any P–O bond cleavage, *i.e.* no phenol was released as a solvolysis product. This result was taken as evidence for the absence of pseudorotation of the initially formed intermediate (**7a**), necessary for the location of the phenoxy group in the apical position (Scheme 4). Since the (**7a**) ⟶ (**7a′**) interconversion involves exchange of groups of comparable apicophilicity (MeO and PhO),[11] the P–N bond cleavage in (**7a**) [formation of (**2a**)] may occur faster than the pseudorotation process.

We have found that the attack of some nitrogen nucleophiles on the substrate (**1a**) can proceed with both ring-opening P–N cleavage and displacement of the PhO group. When (**1a**) was treated with 1 equiv. of *p*-anisidine (*p*-$MeOC_6H_4NH_2$) at room temperature, 2-(*p*-anisidino)-1,3-dimethyl-1,3,2-diazaphospholidine-2,4,5-trione (**1d**) was formed in high yield; the ring-opened product (**2c**) was also isolated from the reaction mixture (Scheme 5). The P–N bond cleavage product (**2c**) could not have been formed by the subsequent reaction of (**1d**) with phenol, since ^1H n.m.r. spectroscopy revealed that (**1d**) remains unaffected by phenol over a long period. We have also found that under refluxing in tetrahydrofuran (THF), (**2c**) can be converted into (**1d**), presumably *via* intramolecular displacement of phenol by the NHMe group. However, we do not believe that the ring closure (**2c**) ⟶ (**1d**) can be responsible for the bulk of (**1d**) formed in the reaction of (**1a**) with anisidine. The product (**1d**) separates from the THF–toluene solution of the substrates almost immediately after mixing, while the ring closure of (**2c**) requires reflux for at least 0.5 h. For the reaction of (**1a**) with anisidine we propose therefore the mechanism indicated in Scheme 6.*

The pseudorotation step converting (**7b**) into (**7b′**), required for the subsequent release of phenol, is in this case encouraged (relative to that shown in Scheme 4) because it involves exchange of ligands (PhO and *p*-$MeOC_6H_4NH$) which differ significantly in their apicophilic preferences. Our results obtained for the reaction of (**1a**) with *p*-anisidine were paralleled by the aminolysis of the same substrate with ammonia. In this case, however, the only product obtained was the ring-retained substitution product, 2-amino-1,3-dimethyl-1,3,2-diazaphospholidine-2,4,5-trione (**1e**) (Scheme 7).

The cyclic product (**1e**) was obtained in yields exceeding 90%, and no P–N bond cleavage product corresponding to (**2c**) was detected. It seems therefore that the pseudorotation of the (**1a**)–ammonia adduct is much faster than endocyclic P–N bond cleavage, so only displacement of the PhO group is observed. In this sense, reactions of (**1a**) with methanol (Scheme 4) and with ammonia (Scheme 7) represent the two extreme cases of nucleophilic displacement at the 1,3,2-diazaphospholidine system, while in the reaction with *p*-anisidine (Scheme 6) substitution at phosphorus follows both available pathways.

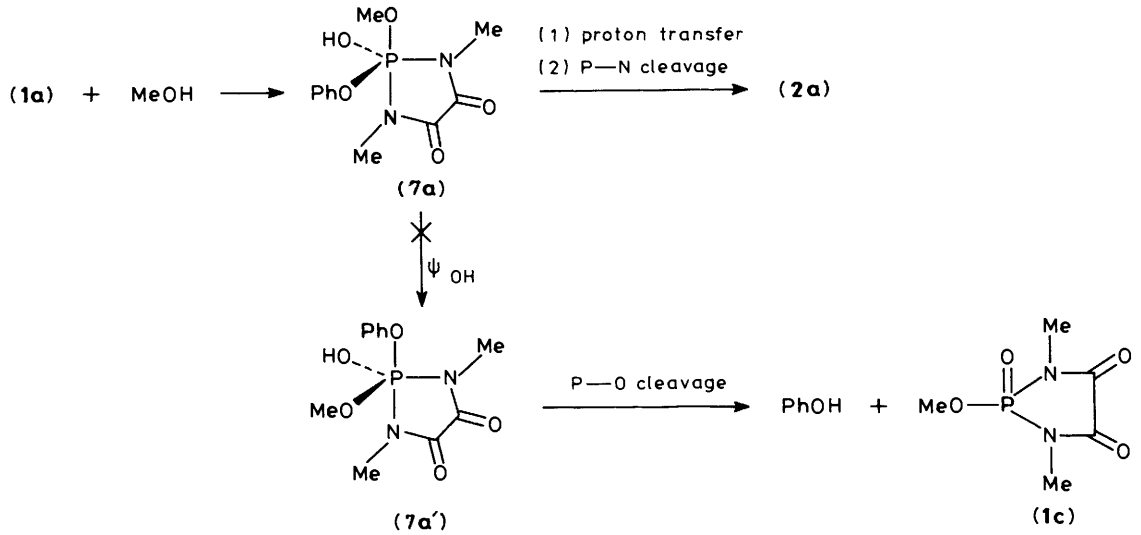
Our results for the reactions of the substrate (**1a**) with *p*-anisidine and ammonia contrast sharply with the aminolysis of (**1a**) reported by Mulliez.[1] While the sterically more hindered amines (such as t-butyl- or dialkyl-amines) or weakly nucleophilic amines (such as *p*-toluidine) were found to be unreactive towards (**1a**), primary alkylamines, such as methyl- or benzyl-amine, reacted with (**1a**) at the carbonyl, *not* the phosphoryl centre. The N–C bond-cleavage, ring-opened product (**8**) underwent subsequent cyclization, *via* displacement of phenol by the carboxamide nitrogen, to give the new 1,3,2-diazaphospholidine (**1f**) with one of the initially endocylic nitrogen atoms in the exocyclic position (Scheme 8).

We have repeated the aminolysis reported by Mulliez for (**1a**), using benzylamine as a nucleophile; in agreement with the earlier report,[1] we obtained the product of initial C–N cleavage, followed by ring closure (**1f**) (R = $PhCH_2$).

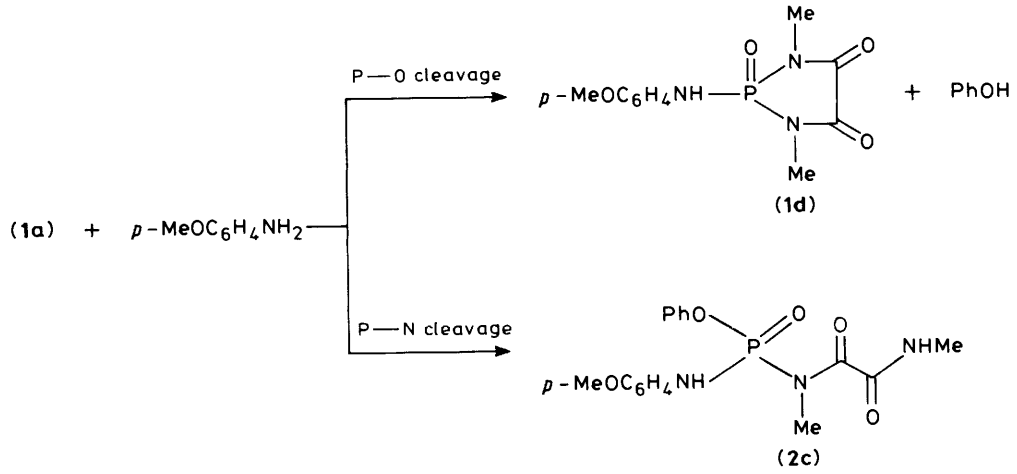
In conclusion, the 1,2,3-trisubstituted derivatives of 1,3,2-diazaphospholidine-2,4,5-trione represent a versatile system which can undergo nucleophilic cleavage according to different mechanistic patterns. Depending on its specific properties, a nucleophile can approach either of the two acyl centres (phosphoryl and carbonyl). In substrates bearing an additional leaving group at phosphorus [as in (**1a**)], substitution at phosphorus can occur with ring-opening P–N bond cleavage or with expulsion of the exocyclic substituent. The detailed structural factors determining the course of these reactions are being investigated in this laboratory.

Molecular Structure of Compound (**1b**) *and Related Compounds.*—The four crystallographically independent molecules yielded structural parameters identical within their standard deviations. The bond lengths and angles reported in Table 1 are hence the average values for the four molecules. When an *N,N′*-dimethyloxamide (**4**) unit is incorporated into a 1,3,2-diazaphospholidine system such as (**1b**), two major structural changes occur. First, the nitrogen atoms now form a part of an imide and not an amide function; secondly, the *trans*-orientation of the α-dicarbonyl linkage in (**4**) is changed to a *cis*-orientation. The amide–imide change in the chemical nature of the nitrogen atoms results in less effective resonance donation of the nitrogen lone pair to the carbonyl group, and hence an increase in the N–C(O) distance. An analogous modification of the N–C(O) fragment caused by the introduction of the phosphoryl group has been observed for the acyclic mixed imide (**5**).[8] However, the most profound changes in the geometry of the oxamide skeleton result from its incorporation into a five-membered phospholidine ring. The ring closure constrains the oxamide N–C(O)–C(O) angle to 109.6°, unusually low for an sp^2 carbon

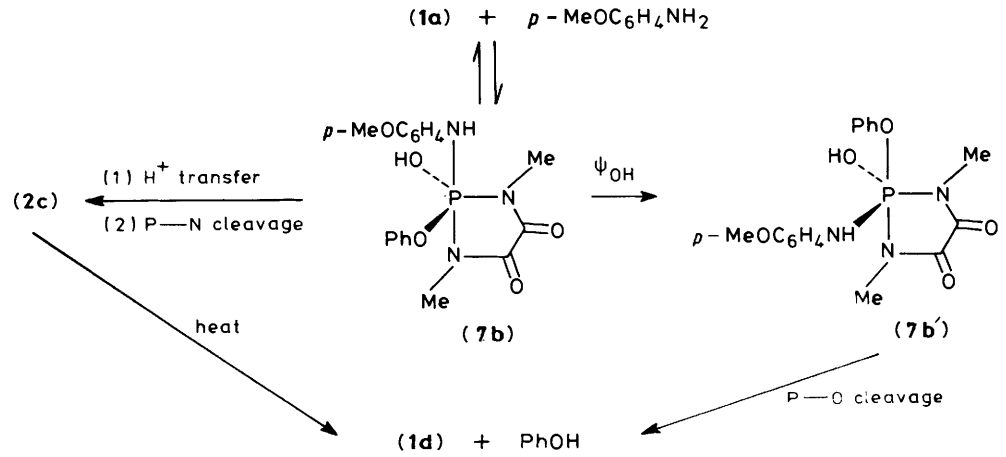
* As a referee has pointed out, the formation of (**1d**) *via* cyclization of (**2c**), as well as the analogous formation of (**1e**) (see Scheme 7), could be catalysed by the base (*p*-anisidine or ammonia, respectively) present in the reaction mixture. We are grateful to the referee for this suggestion, and are investigating this alternative route to products (**1d**) and (**1e**).



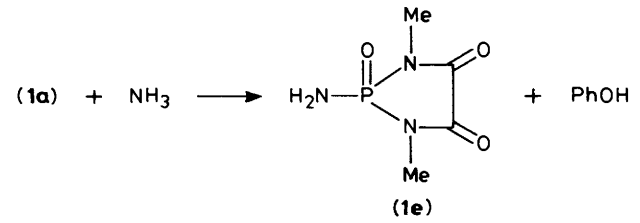
Scheme 4.



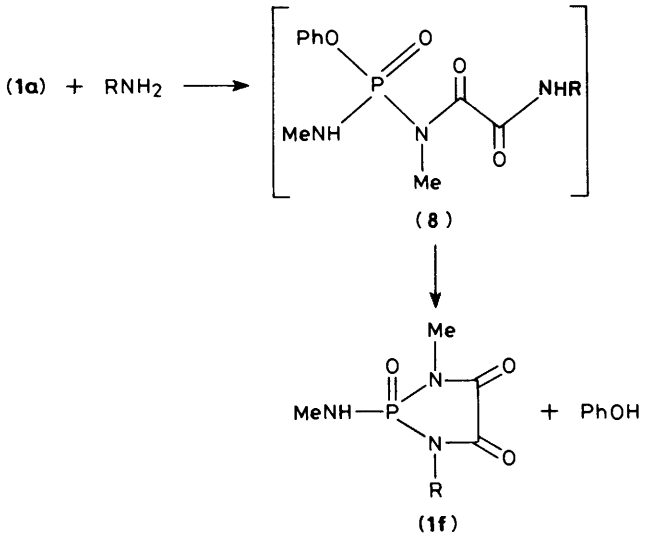
Scheme 5.



Scheme 6.



Scheme 7.



Scheme 8.

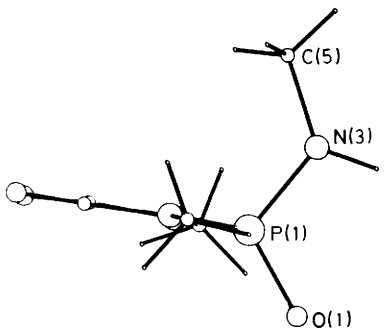


Figure 2. Perspective view of the molecule (**1b**) illustrating the planarity of the phospholidine ring.

atom.* The size of this angle cannot, however, be taken as indicative of any tetrahedral geometry of the carbon atom, because of the planarity of the whole oxamide fragment of the molecule (deviation of carbonyl oxygens from the mean plane of the ring is less than 0.07 Å). The change in the N–C(O)–C(O) angle is accompanied by widening of the O=C–C(O) angle [Δ + 3.3° relative to (**4**)], presumably to minimize steric interactions between the two carbonyl oxygens, the distance between which just exceeds the sum of their van der Waals radii.

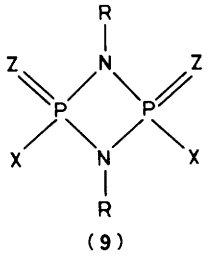
The 1,3,2-diazaphospholidine ring of (**1b**), together with the 4- and 5-oxygen atoms and the 1- and 3-methyl carbon atoms, form an essentially planar system (Figure 2). Table 2 gives the

* Even in a similarly constrained molecule, catechol phosphate, the corresponding O–C–C angle is 111.4°.[12]

Table 2. Deviations (Å) of atoms from the least-squares planes[a] of the 1,3,2-diazaphospholidine ring in (**1b**)

	Deviation (Å)			
Atom[b]	A	B	C	D
P(1)	−0.008	−0.005	0.014	−0.001
N(1)	−0.003	0.003	−0.019	−0.015
N(2)	0.018	0.006	−0.008	0.016
C(3)	0.014	0.000	0.015	0.025
C(4)	−0.020	−0.004	−0.002	−0.026
C(1)	−0.043	−0.022	0.031	0.018
C(2)	−0.011	−0.051	0.063	0.058
O(3)	−0.037	−0.019	0.093	0.095
O(4)	−0.025	−0.040	−0.106	−0.080

[a] Equations of planes: A: $7.0784x + 7.9170y - 4.5633z - 12.5815 = 0$. B: $11.5500x + 3.4334y + 4.5558z - 5.0946 = 0$. C: $16.7212x - 3.2993y + 4.2739z - 10.6943 = 0$. D: $12.3669x + 0.9712y - 4.3205z - 4.0023 = 0$. [b] The atoms italicised were used in the least-squares calculations.



(**9**)

deviations of the nine atoms involved from the least-squares plane of the ring. The coplanarity of the two MeNCO fragments is an obvious consequence of the resonance effects operating within the carboxamide function.[13] The fact that all heavy atoms in (**1b**) (except the two exocyclic substituents at the tetrahedral phosphorus) are essentially coplanar indicates that the phosphorus atom is also involved in specific stereoelectronic interactions with ring nitrogens. The P–N_{endo} distance in (**1b**) (1.67 Å) is significantly shorter than that (1.78 Å) typical of the 'pure' single P–N bond,[14] and not far from the range (1.60—1.66 Å) observed for a variety of phosphoramidates[15] and *N*-phosphorylated sulphoximides,[16] for which a certain amount of P–N π bonding must be considered.

In terms of its bonding to the two endocyclic nitrogen atoms, the phosphorus atom in (**1b**) can be considered as related to the phosphorus atom in cyclodiphosphazenes (**9**). An *X*-ray diffraction study on (**9**); Z = S, X = Cl, R = Me)[17] revealed planarity of the ring, with all four P–N bonds 1.67 Å and the N–P–N angle 84°. This geometry suggests a delocalized π system with maximal overlap between the 2*p* orbitals on N and the 3*d* orbitals on the P atom. We believe that similar stereoelectronic effects operate in (**1b**), where the trigonal geometry of the endocyclic nitrogen atoms, the near planarity of the ring, and the small endocyclic N–P–N angle allow stabilizing interactions between the vacant d_{xz} and d_{yz} orbitals on phosphorus, and the two $2p_z$ non-bonding orbitals of the ring nitrogen atoms.

Intermolecular close contacts involving the exocyclic (amide) nitrogen atoms and the phosphoryl oxygen atoms are in the range 2.951—2.954 Å and may be interpreted in terms of a hydrogen-bonding scheme giving rise to polymeric ribbons of the molecules throughout the structure, as shown in Figure 3.

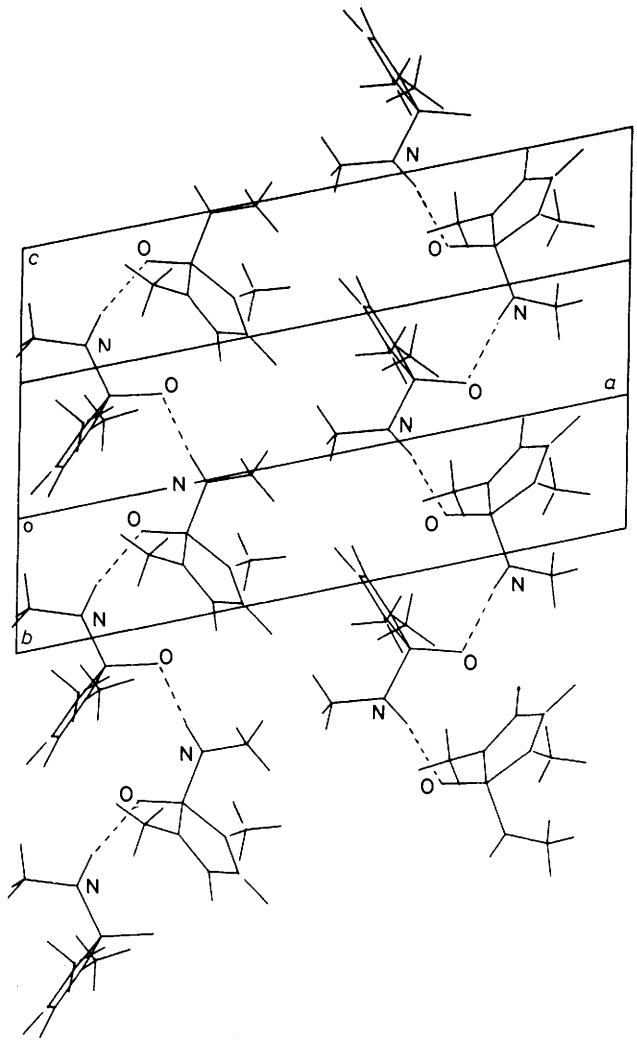


Figure 3. Packing diagram of compound (**1b**); hydrogen bonding is indicated by dashed lines

Table 3. Data pertaining to the crystallographic analysis of (**1b**)

Molecular formula	$C_5H_{10}N_3O_3P$
Space group	$P\bar{1}$
a/Å	18.365(9)
b/Å	13.877(7)
c/Å	7.653(4)
α/°	106.02(2)
β/°	77.99(2)
γ/°	110.17(2)
V/Å^3	1 746
Z	8
D_c/Mg m^{-3}	1.35
μ(Mo-K_α)/mm^{-1}	0.24
F(000)	800
Scan mode	$\omega-2\theta$
Scan width (θ/°)	1.2
Scan speed (° s^{-1})	0.048
θ range (°)	3—24
Stability of standard reflections (%)	1.5
Number of reflections collected	3 458
Number of reflections observed	1 990
Criterion for observed reflections	$I_{rel} > 2\sigma I_{rel}$
Number of parameters	263
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.084
$R_w = \Sigma w^{\frac{1}{2}}\|\|F_o\| - \|F_c\|\|/\Sigma w^{\frac{1}{2}}\|F_o\|$	0.069
Weighting scheme	$(\sigma^2 F)^{-1}$

Experimental

^{1}H N.m.r. spectra were determined with a 100 MHz Varian XL 100 spectrometer, using Me_4Si as internal standard. Mass spectra were recorded with a V6 Micromass 16F spectrometer operating at 70 eV and an ion-source temperature of 200 °C. *N,N',N''*-trimethylphosphoric triamide was prepared as described;[18] m.p. 94—96 °C (from benzene) (lit.,[18] 102—103 °C); $\delta(CDCl_3)$ 2.60 (9 H, d, *J* 12 Hz, 3 NCH_3) and 3.43 (3 H, br s, 3 NH). Phenyl *N,N'*-dimethylphosphorodiamidate was prepared according to the method of Mulliez;[1] m.p. 102—104 °C (from chloroform–ether) (lit.,[1] 103—104 °C); $\delta(CDCl_3)$ 2.62 (6 H, d, *J* 12 Hz, 2 NCH_3), 3.17 (2 H, br s, 2 NH), and 7.2 (5 H, br s, Ph).

Substrates.—Compound (**1a**) was prepared according to the method of Mulliez,[1] as hygroscopic crystals, $\delta(CDCl_3)$ 3.12 (6 H, d, *J* 9 Hz, 2 NCH_3) and 6.90—7.60 (5 H, m, Ph), hydrolysed easily to *N,N'*-dimethyloxamide. Compound (**1b**) was prepared by heating *N,N',N''*-trimethylphosphoric triamide with 1.1 equiv. of oxalyl chloride and 2.2 equiv. of triethylamine in benzene under reflux for 3 h. Triethylammonium chloride was filtered off and washed with hot benzene, and the combined benzene solutions were evaporated under reduced pressure. The crude 1,3-*dimethyl*-2-*methylamino*-1,3,2-*diazaphospholidine*-2,4,5-*trione* was recrystallized from toluene–acetone (2:1); yield, 60%, m.p. 205—207 °C; *m/z* 191 (M^+); $\delta(CDCl_3)$ 2.58 (3 H, d of d, *J* 14 and 5.5 Hz, exocyclic NCH_3), *ca.* 2.9 (1 H, br s, NH), and 3.03 (6 H, d, *J* 9 Hz, 2 endocyclic NCH_3) (Found: C, 31.9; H, 5.5; N, 20.9. $C_5H_{10}N_3O_3P$ requires C, 31.4; H, 5.3; N, 22.0%).

Methanolysis of the Substrate (**1b**).—Compound (**1b**) was dissolved in rigorously dry methanol and stored at room temperature. Samples were withdrawn and evaporated, and the residues dissolved in $CDCl_3$; the ^{1}H n.m.r. spectra were then recorded. No change in the spectrum of (**1b**) was observed after 1 430 h. When the same experiments were carried out at 60 °C or in methanol under reflux, the ^{1}H n.m.r. spectra of the reaction samples showed the presence of increasing amounts of products (**3**) and (**4**). There was no indication of the formation of any other products, which proves that the product of the first step of the reaction was never present in significant quantity. Under reflux conditions, methanolysis was complete after *ca.* 30 min. After cooling, the crystalline product was filtered off, washed with cold methanol, and dried to give the oxamide (**4**) (82%), m.p. (sealed tube) 212 °C (lit.,[19] 217 °C); $\delta(CDCl_3)$ 2.92 (6 H, d, *J* 5 Hz, 2 NCH_3) and 7.57 (2 H, br s, 2 NH) (Found: C, 41.3; H, 6.9, N, 24.1. Calc. for $C_4H_8N_2O_2$: C, 41.4; H, 6.9; N, 24.1%).

The methanolic solution was evaporated under reduced pressure and the residual oil was purified by distillation to give the phosphoramidate (**3**) (63%), b.p. 95—96 °C at 0.5 mmHg (lit.,[20] 81 °C at 1 mmHg); *m/z* 139 (M^+); $\delta(CDCl_3)$ 2.55 (3 H, dd, *J* 11 and 5 Hz, NCH_3), 3.23 (1 H, br s, NH), and 3.68 (6 H, d, *J* 11 Hz, 2 OCH_3) (Found: C, 25.45; H, 7.5; N, 9.95. Calc. for $C_3H_{10}NO_3P$: C, 25.9; H, 7.2; N, 10.1%).

Aminolysis of the Substrate (**1a**).—(i) *Reaction with* p-*anisidine.* *p*-Anisidine was added dropwise at room temperature to a THF–toluene solution of an equimolar quantity of (**1a**) with stirring and exclusion of moisture. The solution was left at room temperature and examined periodically by t.l.c. (Merck, Kieselgel 60; chloroform–acetone, 4:1). After 24 h no substrate was detected and the crystalline product had precipitated. It was filtered off and recrystallized from acetone to give 2-p-*anisidino*-

Table 4. Fractional atomic co-ordinates (× 10^4) for the non-hydrogen atoms of (**1b**)

	A			B			C			D		
	x	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*
P(1)	7 755(2)	9 785(3)	1 451(5)	6 466(2)	8 901(3)	6 629(5)	2 758(2)	4 786(3)	573(5)	1 465(2)	3 902(3)	−4 191(5)
O(1)	7 021(5)	8 909(7)	1 323(11)	7 316(5)	9 158(7)	6 214(11)	2 028(5)	3 913(6)	570(11)	2 318(5)	4 154(7)	−4 365(11)
O(3)	8 274(5)	11 777(7)	5 777(13)	5 481(5)	9 752(7)	11 325(13)	3 275(5)	6 790(8)	−2 280(13)	482(5)	4 756(7)	−7 034(12)
O(4)	9 191(6)	10 357(7)	4 708(12)	5 194(5)	7 501(7)	10 245(12)	4 183(6)	5 353(7)	−3 543(13)	202(5)	2 495(7)	−7 939(13)
N(1)	7 705(6)	10 835(8)	3 186(14)	6 154(6)	9 736(8)	8 418(13)	2 705(6)	5 816(8)	−51(14)	1 157(6)	4 736(8)	−4 853(13)
N(2)	8 473(6)	9 630(8)	2 241(14)	6 001(6)	7 871(8)	7 601(14)	3 478(6)	4 630(8)	−1 111(13)	1 014(6)	2 874(8)	−5 752(13)
N(3)	8 082(6)	10 176(8)	−423(14)	6 046(6)	8 768(8)	4 886(15)	3 078(6)	5 181(9)	2 522(15)	1 052(6)	3 778(8)	−2 188(14)
C(1)	7 147(8)	11 394(11)	3 378(20)	6 384(8)	10 882(10)	8 518(18)	2 148(8)	6 383(11)	878(19)	1 377(8)	5 883(10)	−4 040(18)
C(2)	8 823(10)	8 786(13)	1 381(23)	6 051(9)	6 821(11)	6 761(20)	3 810(9)	3 767(12)	−1 427(21)	1 035(9)	1 807(11)	−6 030(20)
C(3)	8 231(8)	11 076(11)	4 383(20)	5 723(7)	9 295(10)	9 841(18)	3 215(7)	6 073(10)	−1 545(18)	727(8)	4 275(11)	−6 280(18)
C(4)	8 690(8)	10 320(10)	3 857(18)	5 610(8)	8 124(11)	9 341(19)	3 704(8)	5 322(10)	−2 228(19)	601(8)	3 140(11)	−6 778(19)
C(5)	8 780(9)	11 039(12)	−655(21)	5 190(8)	8 494(11)	4 980(19)	3 802(9)	6 042(12)	2 888(21)	205(8)	3 497(11)	−1 674(20)

1,3-*dimethyl*-1,3,2-*diazaphospholidine*-2,4,5-*trione* (**1d**) (60%), m.p. 183—185 °C; δ[$(CD_3)_2SO$] 2.80 (6 H, d, *J* 7 Hz, 2 NCH_3), 3.81 (3 H, s, OCH_3), 7.06 (2 H, d, *J* 9 Hz, 2- and 6-H), and 7.32 (2 H, d, *J* 9 Hz, 3- and 5-H) (Found: C, 43.3; H, 5.3, N, 13.8. $C_{11}H_{14}N_3O_4P{\cdot}H_2O$ requires C, 43.8; H, 5.3; N, 13.9%).

T.l.c. of the filtrate showed the presence of two products, one of which was identified as phenol (R_F 0.56) by comparison with an authentic sample. The second product precipitated out when the partially evaporated solution was left at room temperature for 60 h to give N-[p-*anisodino*(*phenoxy*)*phosphonoyl*]-*N,N'-dimethyloxamide* (**2c**) (18%), m.p. 129—132 °C; δ[$(CD_3)_2SO$] 2.56 (3 H, d, *J* 5 Hz, amide NCH_3), 2.79 (3 H, d, *J* 7 Hz, imide NCH_3), 3.77 (3 H, s, OCH_3), 6.99 (2 H, d, *J* 9 Hz, 2- and 6-H), 7.10—7.40 (8 H, m, 3- and 5-H + Ph + imide NH), and 7.87 (1 H, q, *J* 5 Hz, amide NH) (Found: C, 51.5; H, 5.6; N, 10.5. $C_{17}H_{20}N_3O_5P{\cdot}H_2O$ requires C, 51.6; H, 5.6; N, 10.6%).

When a sample of (**2c**) was heated in THF under reflux for 30 min, and left at room temperature overnight, the ring-closed product (**1d**) precipitated out; yield 90%, m.p. and mixed m.p. 182—184 °C (Found: C, 43.7; H, 5.3; N, 13.5%).

(ii) *Reaction with ammonia.* Dry ammonia was passed at room temperature through a solution of (**1a**) in dry choroform for *ca.* 30 s; then the solution was left at room temperature for 30 min. The white precipitate was filtered off and washed with chloroform. The filtrate was shown (t.l.c.) to contain large quantities of phenol. The precipitate was identified as 2-*amino*-1,3-*dimethyl*-1,3,2-*diazaphospholidine*-2,4,5-*trione* (**1e**) (91%), m.p. 223—227 °C (decomp.); δ[$(CD_3)_2SO$] 2.88 (6 H, d, *J* 9 Hz, 2 NCH_3) and 7.70 (2 H, br s, NH_2); *m/z* 177 (M^+) (Found: C, 26.8; H, 4.8; N, 23.6. $C_4H_8N_3O_3P$ requires C, 27.1; H, 4.6; N, 23.7%).

(iii) *Reaction with benzylamine.* A solution of benzylamine in dry toluene was added to a solution of an equimolar amount of (**1a**) in toluene at room temperature and the mixture was stirred overnight. The precipitate was filtered off, washed with toluene, and dried to give 1-benzyl-3-methyl-2-methylamino-1,3,2-diazaphospholidine-2,4,5-trione (**1f**; R = $PhCH_2$) (30%), m.p. 120—124 °C (lit.,[1] 127—130 °C), δ[$(CD_3)_2SO$] 2.28 (3 H, dd, *J* 15 and 6 Hz, amide NCH_3), 2.93 (3 H, d, *J* 9 Hz, imide NCH_3), 4.67 (2 H, d, *J* 11.5 Hz, CH_2Ph), 5.83 (1 H, m, NH), and 7.50 (5 H, s, Ph) (^1H n.m.r. data almost identical with those in ref. 1).

Crystallographic Analysis of Compound (**1b**).—Accurate unit-cell parameters and a set of *X*-ray data were obtained from a single crystal (0.20 × 0.20 × 0.33 mm) using a Philips PW1100 four-circle diffractometer and Mo-K_α radiation (λ 0.7107 Å). The intensities of three reference reflections were periodically monitored to ascertain crystal stability. Data were corrected for Lorentz-polarization but not for absorption.

The structure was solved using a preliminary version of the direct methods package of SHELXS-84,[21] which yielded all non-hydrogen atoms in an *E*-map. Refinement was carried out using SHELX-76.[22] The phosphorus atoms were treated anisotropically and all others isotropically; methyl groups were treated as rigid with a single temperature factor for all their hydrogen atoms; the amide hydrogen atoms were constrained at 1.00(5) Å from their parent nitrogen atoms, again with a unique temperature factor. In the final refinement, a weighting scheme $(\sigma^2F)^{-1}$ was employed. Details of the data collection and structural refinement are presented in Table 3. Fractional atomic co-ordinates are given in Table 4 (atom numbering is shown in Figure 1).

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