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Phosphoric triamides. ^{31}Phosphorus NMR chemical shift as a function of the P–N bond characteristics

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Six phosphoric triamides in which amide nitrogens are incorporated into an increasing number (from 0 to 3) of the 1,3,2-diazaphospholidin-2-one rings have been prepared and their crystal structures have been determined. The structural changes from the non-cyclic to the mono-, di- and tri-cyclic systems result in the decrease of the N–P–N bond angles and the increase of the P–N bond distance. These changes are paralleled by a strong deshielding of the ^{31}P nucleus, leading to an exceptionally high δ_P value for the tricyclic derivative. The δ_P–structural parameters relationship is discussed in terms of the changes in hybridization of phosphorus and the variation in the P–N bond order.

The major contribution to the ^{31}P NMR chemical shift results from the paramagnetic term,[1] not easily accessible by theoretical calculations.[2] The average excitation energy approximation leads to the equation linking the chemical shift with the changes in bond overlap and hybridization. According to Letcher and Van Wazer,[3] the ^{31}P chemical shift differences, $\Delta\delta$, are dominated by three terms affected by structural variations, eqn. (1), where $\Delta\chi$ is the difference in electronegativity in the

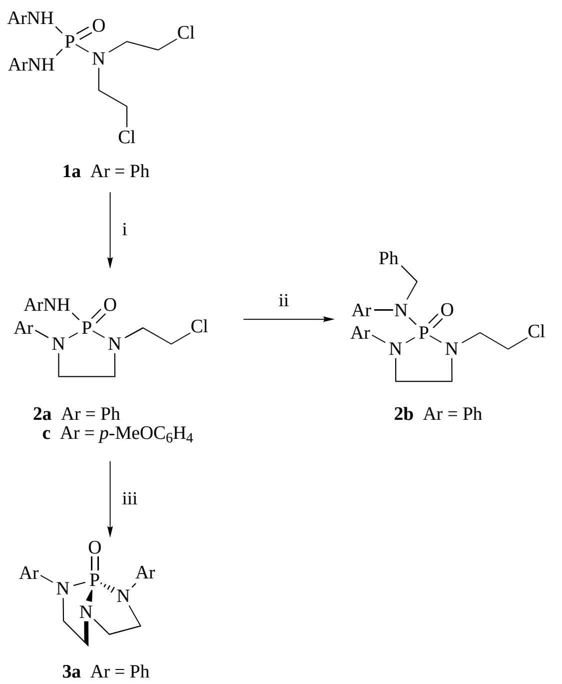
$$\Delta\delta = -C\,\Delta\chi_X + k\,\Delta n_\pi + A\,\Delta\theta \qquad (1)$$

P–X bond, Δn_π the change in the π-electron overlap, $\Delta\theta$ the change in the X–P–X σ bond angle, and C, k and A are constants. In his extensive work on the applications of ^{31}P NMR spectroscopy,[4] Gorenstein focussed on the sensitivity of the heavy-atom chemical shifts to bond angle changes[5] and proposed an empirical correlation between ^{31}P chemical shifts and the O–P–O bond angles in phosphates. According to that principle, a decrease in the O–P–O bond angle results in a deshielding of the phosphorus nucleus; ionization of the phosphate function or the nature of the ester groups at phosphate oxygens being of much lesser importance. As a consequence of the relationship, cyclic five-membered ring phosphate esters, with the endocyclic O–P–O bond angle less than 100°, are shifted downfield from their acyclic counterparts by up to 20 ppm.[6] It is well known that the same substrates are several orders of magnitude more reactive in the nucleophilic cleavage of the P–O bond than the acyclic analogues;[7] the magnitude of the ^{31}P NMR chemical shift can therefore be related to the reactivity of the phosphoryl centre.

In our studies on the structure–reactivity relationship in phosphoric amides, we attempted to relate the solvolytic reactivity of the *endo-* *vs.* *exo*-cyclic P–N bond in cyclic phosphoric triamides to the ^{15}N NMR parameters of the substrates.[8] All compounds studied there were however non-crystalline (oils), so their molecular parameters (bond distances and angles) were not easily accessible. In our recent preparation of phosphoric triamides,[9] we have synthesized several structurally closely related, crystalline products, suitable for X-ray diffraction studies. Using our procedures, as well as some literature methods, we have now prepared a series of phosphoric triamides in which the main structural difference involves sequential incorporation of the triamide nitrogens into the five-membered 1,3,2-diazaphospholidin-2-one ring systems. The effect of the structural modifications on the shielding of the phosphorus atom was then determined by ^{31}P NMR spectroscopy, and the δ_P values were correlated with the molecular parameters of the three P–N bonds of the triamide function.

Results and discussion

The representatives of the first three groups of substrates studied (**1**, **2**, **3**) are interrelated by a sequence of 1,5-cyclization reactions given in Scheme 1. The monocyclic phosphoric triamide **2a** was additionally *N*-benzylated to a crystalline derivative **2b** in order to evaluate any possible effect of intermolecular hydrogen bonding on the molecular parameters in the solid state.[10] The tricyclic amidate **4** was prepared after some modifications of the literature procedure (Scheme 2).[11]

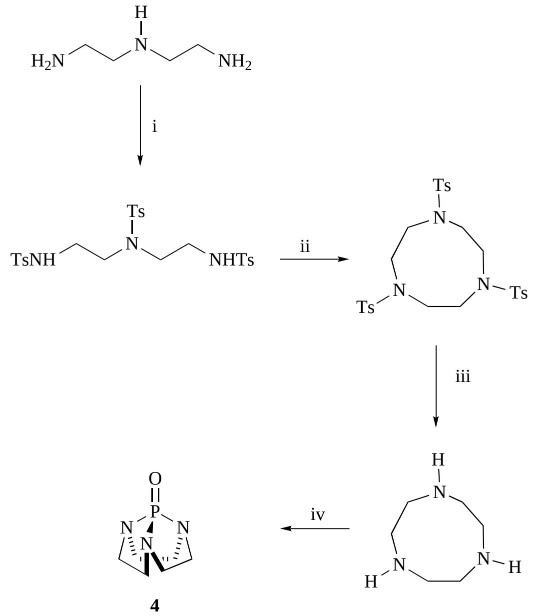


Scheme 1 *Reagents and conditions*: i MeONa–MeOH (95%); ii NaH, PhCH$_2$Br, Bu$_4$NBr, C$_6$H$_6$ (77%); iii NaH, C$_6$H$_6$ (90%)

Table 1 Structural and spectroscopic data for amides **1**–**4**

Compound	δ_P[a]	P=O/Å	P–N/Å	N–P–N/°
1a	4.3	1.464(3)	1.636(4) 1.638(4) 1.644(4)	106.7(2) 103.4(2) 107.0(2)
2a	13.4	1.477(2)	1.637(2) 1.646(2)[b] 1.656(2)[b]	110.7(2) 111.6(2) 94.3(2)[c]
2b	17.2	1.473(3)	1.629(3) 1.669(3)[b] 1.644(3)[b]	108.8(2) 109.0(2) 93.3(2)[c]
2c	14.7	1.477(2)	1.627(2) 1.645(2)[b] 1.660(2)[b]	110.4(11) 111.2(11) 93.6(11)[c]
3a	33.5	1.437(5)	1.653(6) 1.661(6) 1.676(6)	114.4(3) 96.2(3) 95.7(3)
4	98.0	1.481(4)	1.663(4) 1.678(4) 1.680(4)	101.0(2) 101.2(2) 100.5(2)

[a] In $CDCl_3$, 30 °C; concentration 0.2 M. [b] Endocyclic P–N bond. [c] Endocyclic N–P–N bond angle.



Scheme 2 *Reagents and conditions*: i TsCl, pyridine (75%); ii EtONa–EtOH, then $TsOCH_2CH_2OTs$ (94%); iii H_2SO_4, then aq. NaOH (65%); iv $P(O)Cl_3$, Et_3N (16%)

The compound proved to be highly unstable and decomposed easily, so the determination of its crystal structure presented some problems (see Experimental section). The required molecular parameters were however successfully determined, and the reactivity of **4** will be published elsewhere.[12] The structural and spectroscopic data required for the discussion are collected in Table 1. The first obvious result is a rather powerful deshielding effect ($\Delta\delta_P = +93.8$ ppm) of the structural changes in the sequence **1**→**4** on the ^{31}P NMR chemical shift. The typical range for the δ_P values observed for the compounds in which the phosphoryl function is bonded to three nitrogen atoms is between −5 and+26; the only exception reported in a recent compilation of the ^{31}P NMR data and including 23 examples,[13] is compound **4**, for which a value of $\delta_P = 41$ was reported by Verkade and co-workers.[11] When preparing compound **4**, we have found however that the value of the ^{31}P NMR chemical shift for the product which was also used for X-ray diffraction study is, in fact, $\delta_P = 98.0$, much higher than that reported in the literature.[11] We have observed occasionally in the ^{31}P NMR spectra of crude **4** a signal of $\delta_P \approx 40$, probably derived from the decomposition of **4** and taken by the authors of the report as a true value for the tricyclic compound.

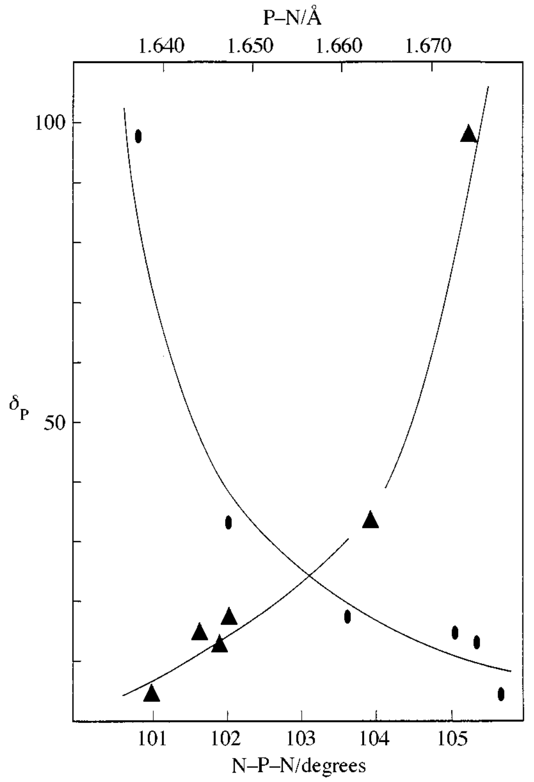


Fig. 1 Effect of structural parameters on the ^{31}P NMR chemical shift of phosphoric triamides. ▲, δ_P *vs.* P–N bond distance; ▮, δ_P *vs.* N–P–N bond angle.

Since the nature of the atoms bonded to phosphorus (N,N,N,O) is constant for all compounds studied, and since the type of the nitrogen substitution (aromatic or aliphatic substituents) is the same for the first three types (**1**, **2**, **3**), it may be concluded that the observed deshielding effect results not from any effective electronegativity changes [$\Delta\chi_x$ term in eqn. (1)], but from the changes in the nature of the P–N bonding that follow the changes in the molecular geometry. This conclusion can be corroborated by a comparison of the δ_P value for **4** (98.0) with that of $\delta_P = 23.3$ reported for hexaethylphosphoric triamide, $(Et_2N)_3PO$.[14] For that pair of phosphoric triamides any differences in the polar effects of the substituents can certainly be ignored, and the dramatic deshielding effect of 74.7 ppm must reflect solely the difference in the geometries of the molecules.

A convincing trend of the ^{31}P NMR downfield shift with the decrease in the O–P–O bond angle in the PO_4 tetrahedra has been demonstrated by Gorenstein for a large number of systems,[6] and associated with the changes in the hybridization resulting from the bond angle changes.[5] A much poorer correlation involving a few selected substrates was reported for the S–P–S bond angle variations,[15] and, to our knowledge, in only one case the downfield shift of the δ_P value in cyclic phosphorus(III) triamides (P^{III} derivatives) upon moving from the six-membered to the five-membered system was reported.[11] Following these approaches, we have related the δ_P values for compounds **1**–**4** to the average value of the three N–P–N bond angles present in each molecule. The result is presented in Fig. 1. The results obtained for the P–N bonding case fully confirm earlier observations derived from the phosphate systems, and they demonstrate that even within a narrow range of structurally closely related substrates, variations in the geometry can lead to formidable changes in the shielding parameters at the phosphoryl centre. The observed effect prompted us to analyse the change in the molecular parameters within the series in more detail.

The N–P–N bond angle decreases along the series indicating the shift of the hybridization of the phosphorus–nitrogen bond-

Table 2 Typical P–N bond distances for organophosphorus compounds containing nitrogen

Compound or class of compounds	Hybridization	P–N/Å	Reference
$^{-}HO_3P{-}NH_3^{+}$ [a]	sp^3	1.77	17
$>P(O){-}N<$ [a]	sp^3–sp^2	1.61–1.65	18
$>P(NR){-}N<$ [a]	sp^2	1.52–1.60	19
P≡N [b]	sp	1.49	20

[a] Determined by X-ray diffraction. [b] Determined by gas-phase spectroscopy.

ing orbitals from the sp^3 towards the unhybridized, p^3 (pyramidal) state. Such a trend should have a profound effect on other properties of the P–N bonding, such as bond length, hence the stability. For any covalent bond the less s-character in a hybrid atomic orbital (AO), the further it lies from the bonded nuclei.[16] Examination of the available data on the P–N bond distances in various classes of organophosphorus compounds allowed us to arrange them into groups according to the decreasing P–N bond length resulting from the increasing s-character in the bonding orbital (Table 2). The variations in the bond length are large, and our value of the average P–N distance of 1.674 Å obtained for **4** locates this compound beyond the usual range of values observed for phosphoric triamides. The gradual decrease in the N–P–N bond angles is paralleled therefore by the stretching of the P–N bond towards the value obtained for the 'pure' single bond in the zwitterionic form of phosphoramidic acid, $^{-}HO_3P{-}NH_3^{+}$. A similar relationship between the bond angles and distances was reported before for a pair of cyclic phosphate esters with the P–OAr group located in the equatorial or the axial position.[21] The contraction of the endocyclic O–P–O bond angle in the equatorial stereoisomer (104.8 *vs.* 107.9°) was followed by the endocyclic P–O bond distance increase to an average of 1.565 relative to 1.554 Å in the axial isomer. When the average P–N bond distances obtained for the series **1**–**4** were used for the correlation with the δ_P values, a plot mirroring that obtained for the N–P–N bond angle effect was obtained (Fig. 1). It is, to our knowledge, the first direct correlation of a P–X bond distance with the ^{31}P NMR shielding, and we propose it as a better measure of the effect of structural parameters on the NMR characteristics. The increase in the pyramidality of the N_3P fragment of the phosphoric triamide tetrahedron results in the increase of the P–N bonding distance (more 'p' character in the bonding orbital), which in turn reduces the P–N bond order by reducing the $p \rightarrow d$ π back-donation to the phosphoryl centre. When not all nitrogen atoms are incorporated into the 1,3,2-diazaphospholidin-2-one skeleton, the exocyclic P–N bond is capable of compensating partially for the effect of the hybridization change of the endocyclic nitrogens by increasing the conjugation of the exocyclic nitrogen lone pair with phosphorus. This can be clearly seen for substrates **2**, for which the exocyclic P–N bond is always significantly shorter than the two endocyclic bonds. The extreme situation is achieved in **4** where all three nitrogens are located in the bridgehead positions shared by three phospholidine rings. In this molecule no 'compensation' is possible, all N–P–N bond angles are small and all P–N bond distances large (all nitrogens approach the 'p^3' character), and no significant $p \rightarrow d$ π back-donation from nitrogens can be expected. Such a geometry of a triamide is associated with a dramatic deshielding of the ^{31}P nucleus, as demonstrated by the unusually high value of the chemical shift, well beyond the range expected for the unstrained amides of phosphoric acid.

It may be concluded therefore that the two last terms in eqn. (1) should not be treated independently, since the variations of the latter affect the former *via* the change in the π-electron overlap between nitrogen and the phosphorus nuclei. The $\Delta\delta_P$ *vs.* P–N bond distance plot (Fig. 1) leads to speculation that the extrapolation of the plot to the non-bonded P–N distances (full removal of the P atom from the bonding sphere of nitrogens) should indicate the limiting δ_P value (highly positive) for the PO^+ ion, inaccessible for direct measurement, but a common species in the mass spectra of organophosphorus compounds.[22]

Experimental

Solvents and commercially available substrates were purified by conventional methods. NMR spectra were recorded on a Bruker AC 300 spectrometer in $CDCl_3$, and the chemical shift values are given in ppm relative to the solvent (^1H, δ 7.24), or to 85% H_3PO_4 (^{31}P, δ 0.00) as external standard. *J* Values are given in Hz.

Preparation of substrates

Preparation of **1a**, **2a**, **2c** and **3a** has been described before.[9]

3-(2-Chloroethyl)-1-phenyl-2-(*N*-benzyl-*N*-phenylamino)-1,3,2-diazaphospholidin-2-one 2b. To a solution of **2a** (0.50 g, 1.49 mmol) and phenylbromomethane (0.34 ml, 2.98 mmol) in THF (15 ml), NaH (0.053 g, 2.23 mmol) and Bu_4NBr (0.025 g) were added and the mixture was stirred overnight at room temperature. The reaction mixture was poured on ice-cold aq. NH_4Cl (30 ml) and extracted with $CHCl_3$ (3 × 10 ml); the chloroform solution was dried ($MgSO_4$), evaporated and the crude product was purified by column chromatography (SiO_2, diethyl ether). Yield 0.49 g (77%); colourless solid, mp 103–104.5 °C. $\delta_P(CDCl_3)$ 17.2; δ_H 2.95 (2H, m), 3.30 (4H, m), 4.42 (1H, dd), 4.98 (1H, dd), 6.68 (2H, m), 6.97 (1H, t), 7.08 (7H, m), 7.16 (3H, m), 7.25 (2H, t) (Found: C, 64.83; H, 6.00; N, 9.86. $C_{23}H_{25}N_3ClOP$ requires: C, 64.86; H, 5.88; N, 9.87%).

1,4,7-Tritosyl-1,4,7-triazaheptane.[23] A solution of bis(2-aminoethyl)amine (20.6 g, 0.20 mol) in pyridine (30 cm^3) was added dropwise to a solution of toluene-*p*-sulfonyl chloride (115 g, 0.6 mol) in pyridine (300 cm^3) at such a rate that the temperature of the reaction mixture was maintained at 50–60 °C. The solution was stirred at that temperature for an additional 30 min, cooled to room temperature, and water (100 cm^3) was slowly added. The mixture was stirred overnight, cooled in ice and the white precipitate was filtered off, washed with ice-cold 95% ethanol and dried at 100 °C under reduced pressure. Purified by crystallisation from acetonitrile. Yield 82.9 g (75%); mp 173–175 °C (lit.[23] mp 174-175 °C).

1,4,7-Tritosyl-1,7-disodium-1,4,7-triazaheptane.[11,24] A solution of tritosyl triamine (75 g, 0.132 mol) in anhydrous ethanol (330 cm^3) was heated to reflux, the heat source was removed and a solution of sodium ethanolate (prepared from 34.5 g of sodium in 260 cm^3 of anhydrous ethanol) was added in an atmosphere of dry nitrogen as rapidly as possible. The solution was decanted and left overnight; the precipitated disodium derivative was filtered off under nitrogen, washed with ice-cold ethanol, then with diethyl ether and dried at 100 °C under reduced pressure. Yield 79.1 g (98%). The product was used for the next reaction without further purification.

1,4,7-Tritosyl-1,4,7-triazacyclononane.[24] A solution of the disodium derivative (79 g, 0.129 mol) in anhydrous DMF (530 cm^3) was heated under dry nitrogen to 100 °C and a solution of 1,2-bis(toluene-*p*-sulfonyl)ethane (prepared by tosylation of ethane-1,2-diol with tosyl chloride in pyridine; 77%; 48.1 g, 0.129 mol) in DMF (270 cm^3) was added slowly with stirring. The solution turned turbid and yellow; it was stirred for an additional 1 h at 100 °C, and cooled to room temperature. The solution was then added to vigorously stirred water (2500 cm^3), the precipitate was filtered off, washed with water (500 cm^3) and dried at 80 °C under reduced pressure. Yield 72 g (94%); mp 219–223 °C (lit.[24] mp 217–223 °C); δ_H 2.41 (9H, s, 3 × Me of Ts), 3.40 (12H, s, 6 × CH_2), 7.23 (12H, two d, 3 × C_6H_4).

1,4,7-Triazacyclononane. The tritosyl derivative (20 g, 33.8 mol) was dissolved in conc. H_2SO_4 (10 cm^3) and the mixture was

Table 3 Crystal and data collection details

	1a	**2b**	**3a**	**4**
Empirical formula	$C_{16}H_{20}Cl_2N_3OP$	$C_{23}H_{25}ClN_3OP$	$C_{16}H_{18}N_3OP$	$C_6H_{12}N_3OPH_2O$
Formula weight	372.22	425.88	299.30	191.20
Space group	$P2_1/c$	$P2_1/c$	P_{bca}	$P2_1/c$
a/Å	11.785(2)	9.176(2)	6.235(3)	23.109(9)
b/Å	18.564(2)	9.799(2)	18.758(6)	7.119(1)
c/Å	8.70(1)	24.913(4)	25.688(9)	10.901(2)
β/°	104.52(1)	91.59(1)	90	103.35(3)
V/Å^3	1843(2)	2239.2(8)	3004(2)	1744.9(8)
Z	4	4	8	8
F(000)	776	896	1264	816
μ(Mo-Kα)/mm^{-1}	0.446	0.261	0.185	0.280
Crystal dimensions/mm	0.20 × 0.20 × 0.20	0.15 × 0.15 × 0.18	0.15 × 0.15 × 0.25	0.10 × 0.12 × 0.30
D_c/g cm^{-3}	1.341	1.263	1.323	1.455
θ range scanned/°	1–25	1–25	1–25	1–25
Range of h, k, l	13, −22, ±10	±10, 11, 29	7, 22, 30	27, −8, ±12
Decay of std reflns (%)	2.8	<1	1.2	5.8
Absorption correction:				
Min, max, ave, correction	0.953, 0.999, 0.983	0.952, 0.997, 0.971	^{a}	0.660, 0.999, 0.796
No. reflections collected	3234	3723	2645	3071
No. reflections with $I_{rel} > 2\sigma I_{rel}$	1977	1487	915	1611
No. parameters	236	271	191	237
Max LS shift to esd	0.020	0.007	0.000	0.114
$R1$ ($I > 2\sigma I$)	0.0674	0.0547	0.0898	0.0630
$wR2$ (all data)	0.2393	0.1296	0.2687	0.1798
Goof on F^2	1.031	0.839	0.809	0.941
Max, min residual electron density/e Å^{-3}	0.55, −0.62	0.22, −0.24	0.53, −0.75	0.36, −0.47

[a] An absorption correction was not applied to this crystal.

heated with stirring at 120 °C for 120 h. After cooling the solution was neutralized by slow addition of aq. NaOH (240 g in 500 cm^3 water) and left overnight at 0 °C. The supernatant solution was decanted from the precipitated Na_2SO_4 and extracted in a continuous extraction apparatus with chloroform (350 cm^3) for 3 days. Sodium sulfate was additionally extracted with chloroform (200 cm^3) and the combined chloroform solution was evaporated on a rotary evaporator. The residue was dissolved in benzene (4 × 50 cm^3), the combined benzene solution was dried (Na_2SO_4), and the solvent was removed under reduced pressure. The crude product (viscous oil) was purified by bulb-to-bulb distillation, oven temp. 40 °C/0.1 mm. Colourless oil, 2.83 g (65%); δ_H 1.81 (3H, s, 3 × NH), 2.78 (12H, s, 6 × CH_2). Lit.[25] δ_H 1.83 (3H, s), 2.82 (12H, s).

10-Oxo-10-phospha-1,4,7-triazatricyclo[5.2.1.0^{4,10}]decane 4.[11] A solution of phosphoryl chloride (1.19 g, 7.8 mmol) in benzene (24 cm^3) was added over a period of 1 h with stirring to an ice-cooled solution of 1,4,7-triazacyclononane (1.0 g, 7.7 mmol) and triethylamine (2.34 g, 23.2 mmol) in benzene (50 cm^3). The mixture was stirred at room temperature for 2 h, filtered under dry nitrogen, and the precipitate was washed with benzene (200 cm^3). The combined benzene solution was evaporated under reduced pressure yielding a crude product which was purified by crystallization from boiling benzene–hexane–CH_2Cl_2. White crystals, 0.21 g (16%); mp 212–215 °C (dec) (lit.[11] mp 215 °C, dec); δ_P($CDCl_3$) 98.0; (C_6D_6) 93.8 (lit.[11] δ_P 41) (Found: C, 38.35; H, 7.36; N, 21.72. $C_6H_{12}N_3OP{\cdot}H_2O$ requires C, 37.69; H, 7.38; N, 21.98%).

Structure determination

Crystal and molecular structures of **2a** and **2c** have been described before.[26]

Sample preparation and data collection. Single crystals of **1a**, **2b** and **3a** were selected and mounted on the end of a glass fibre using cyanoacrylate glue. Compound **4** was very unstable in air and was covered in glue before it was mounted in a Lindemann capillary which was then sealed with glue. Data were collected on an Enraf–Nonius CAD4 diffractometer at 293 K using graphite monochromated Mo-Kα radiation ($\lambda = 0.7107$ Å). Accurate cell parameters were obtained by least-squares analysis of the setting angles of 24 reflections in the range $16° \leqslant \theta \leqslant 17°$. The $\omega/2\theta$ mode was used at a maximum recording time of 40 s. The scan width chosen was (0.85 + 0.35 tan θ) and an aperture width of (1.12 + 1.05 tan θ) and a vertical aperture length of 4 mm were used. Three standard reflections were checked periodically for intensity and orientation control. Data were corrected for Lorentz-polarization and absorption effects.

Structure solution and refinement. Structures of **1a**, **2b**, **3a** and **4** were solved by direct methods using SHELXS86.[27] They were refined by full matrix least squares on F^2 using SHELXL93.[28] All non-hydrogen atoms were refined anisotropically. Unless otherwise stated, hydrogens were placed in calculated positions and linked to common isotropic temperature factors. The carbons of one chloroethyl chain in **1a** were disordered over two positions and were refined with site occupancies of 0.61 and 0.39. Hydrogens attached to N(2) and N(3) on this molecule were located in difference electron density maps and modelled independently, but with a distance restraint on the N–H bond length. The benzyl hydrogens of **2b** were located in a difference electron density map and refined independently. Compound **4** crystallized with two independent molecules and two water molecules in the asymmetric unit. The water hydrogens were located in the difference electron density map and allowed to refine independently. Further details are given in Table 3.

Molecular and crystal structures

Full crystallographic details, excluding structure factor tables, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme, see ‘Instructions for Authors’, *J. Chem. Soc.*, *Perkin Trans. 2*, available *via* the RSC Web pages (http://chemistry.rsc.org/rsc/p1pifa.htm). Any request to the CCDC for this material should quote the full literature citation and the reference number 188/109.

Fig. 2(*a*) shows the molecular structure of **1a**. One of the ethyl chains is disordered as shown. The molecule is held in a fairly rigid conformation by two intramolecular hydrogen bonds [C(22)–H(22) · · · N(3) and C(32)–H(32) · · · O(1)]. Molecules pack in layers parallel to [001], held in place by N–H · · · O hydrogen bonding. These layers in turn pack head-to-tail

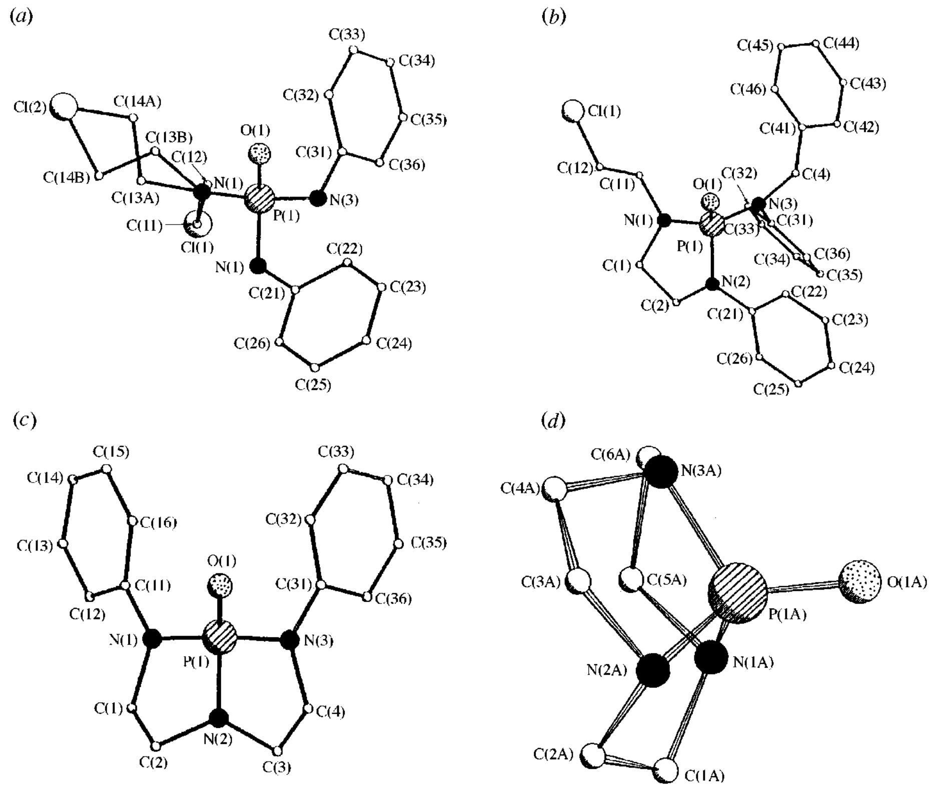


Fig. 2 Molecular structures of **1a**, **2b**, **3a** and **4**

Table 4 Intra- and inter-molecular contacts

	D···A/Å	D–H/Å	D–H···A/Å
1a			
N(2)–H(2)···O(1)^a	2.857(5)	0.816(35)	164(4)
C(22)–H(22)···N(3)	3.350(6)	0.930(7)	119.5(1)
C(32)–H(32)···O(1)	2.509(5)	0.930(7)	129.3(1)
C(14)–H(14)···Cl(2)^a	2.80(4)	0.97(5)	155.0(6)
C(34)–H(34)···Cl(2)^b	2.968(7)	0.930(9)	158.5(2)
2b			
C(4)–H(4)···O(1)	2.941(5)	0.92(3)	116(2)
3a			
C(16)–H(16)···O(1)	3.165(9)	0.93(1)	131.3(7)
C(32)–H(32)···O(1)	3.114(9)	0.93(1)	130.2(8)
4			
O(1W)–H(1W)···O(1A)	2.883(6)	0.95(8)	172(6)
O(1W)–H(2W)···O(2W)^c	2.992(8)	1.16(8)	165(6)
O(2W)–H(3W)···O(1B)	2.909(6)	1.16(9)	156(6)
O(2W)–H(4W)···O(1W)	2.949(8)	0.94(9)	145(8)

^{a} *via* $x, \frac{1}{2} - y, z - \frac{1}{2}$. ^{b} *via* $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$. ^{c} *via* $x, 1\frac{1}{2} - y, z - \frac{1}{2}$.

parallel to [010], with two weaker intermolecular contacts between layers [C(14B)–H(14D)···Cl(2) and C(34)–H(34)···Cl(2)]. Details of the intermolecular contacts are given in Table 4.

Compound **2b** also contains one intramolecular C–H···O hydrogen bond, involving one of the benzyl hydrogens [Fig. 2(*b*) and Table 4]; the molecules pack head-to-tail in layers parallel to [001].

Compound **3a** is shown in Fig. 2(*c*). The two 1,3,2-diazaphospholidine rings are in the envelope conformation, with C(10) and C(4) above the ring in each case. The phenyl rings are almost coplanar with the five-membered rings [angles between rings are 33.8(4) and 23.8(4)°]. Two weak intramolecular C–H···O hydrogen bonds hold the molecule in this cup-shaped conformation. Details are given in Table 4. The molecules pack in herringbone fashion.

Compound **4** was unusual in this series because it was found to be very unstable. The crystal structure revealed another unusual feature—the inclusion of water molecules in the solid stucture.† Fig. 2(*d*) shows the molecular structure of **4**. As expected, this molecule is very rigid. Each five-membered ring is in the envelope conformation, with C(1), C(3) and C(6) the atoms out-of-plane of each ring respectively. The molecules pack in layers parallel to [001] with a layer of water molecules interleaved between the layers of **4**. The structure is held together by an infinite network of O–H···O hydrogen bonds. Details are given in Table 4.

Acknowledgements

Financial assistance from the University of Pretoria, University of Cape Town, and the Foundation for Research Development is gratefully acknowledged.

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† The relationship between the molecular structure of **4** and its chemical behaviour will be published separately.[12]

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Paper 7/04966H
Received 10*th July* 1997
Accepted 25*th September* 1997