Synthesis and *X*-Ray Crystal Structure of the Bis(imino) Cyclodiphosphazane, $[(PhN)P(NMe_2)(NPh)]_2$†‡

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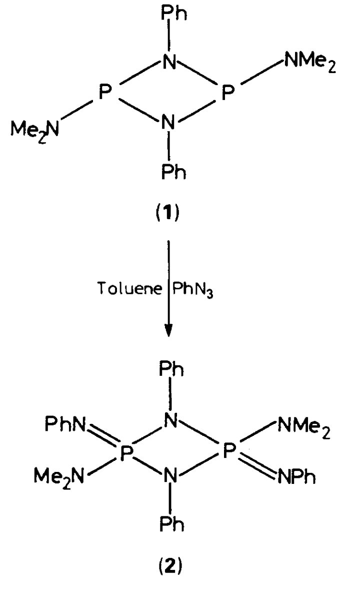
The reaction of *trans*-$[(PhN)P(NMe_2)]_2$ (**1**) with 2 equivalents of phenyl azide yields the bis(imino) derivative, *trans*-$[(PhN)P(NMe_2)(NPh)]_2$ (**2**). The *X*-ray crystal structure of (**2**) reveals that the N_2P_2 ring and the phenyl groups attached to the ring nitrogen atoms are coplanar. The ring nitrogen atoms as well as the nitrogen atoms of the dimethylamino groups display trigonal planar geometry. The bond length of 1.518 Å for the exocyclic P=N bond indicates that this bond is not delocalised with the N_2P_2 ring system.

Structural features of four-membered N_2P_2 ring compounds in which the co-ordination number of phosphorus varies from three to five have attracted considerable attention in recent years.[1–3] Structural studies have been carried out on 1,3,2,4-diazadiphosphetidines containing exocyclic P=O, P=S, and P=Te bonds.[2,4–6] Although several 1,3,2,4-diazadiphosphetidines containing exocyclic P=N bonds have been reported in recent years,[7] no *X*-ray crystal structure analysis has been reported. Only the *X*-ray crystal structures of an anionic cyclodiphosphazane,[8] $[Re(CO)_3\{(RN)_2P_2(NR_2)(NR)_3\}]$ (R = Me_3Si), and a cationic derivative with an exocyclic P=N bond,[9] $[Me_2Si(NR)_2P(NR)_2P(NR)(NHR)]^+[Re_2(CO)_6(\mu\text{-}Cl)_3]^-$ (R = Me_3Si), have been reported. We now report the synthesis and structural analysis of a bis(imino)cyclodiphosphazane and compare its structural features with those of $[(Pr^i_2N)_2P{=}N]_2$, the first cyclodiphosphazene isolated by Baceiredo *et al.*[10]

Results and Discussion

Reaction of *trans*-$[(PhN)P(NMe_2)]_2$, (**1**),[11] with PhN_3 in boiling toluene affords *trans*-$[(PhN)P(NMe_2)(NPh)]_2$ (**2**). The i.r. spectrum of (**2**) exhibits a band at 1 365 cm^{-1} which is assigned to the exocyclic P=N vibration. The ^1H n.m.r. spectrum shows only a single doublet at δ 2.65 (J_{PH} = 11 Hz) for 'NMe₂' protons indicating the presence of only one isomer. The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum consists of a singlet at δ −23.6 p.p.m. A single-crystal *X*-ray analysis reveals the *trans* configuration of the dimethylamino and consequently the phenylimino groups (see below). Thus the Staudinger reaction of the diazadiphosphetidine (**1**) proceeds with net retention of configuration at the phosphorus centres.



(**1**)

(**2**)

Table 1. Selected structural parameters (lengths in Å, angles in °) for $[(PhN)P(NMe_2)(NPh)]_2$ (**2**)

P–N(1)	1.518(2)	P–N(3)	1.625(2)
P–N(2)	1.699(2)	P···P′	2.574(1)
P–N(2′)	1.698(2)		
N(1)–P–N(2)	121.4(1)	P–N(2)–C(21)	130.8(2)
N(1)–P–N(3)	107.8(1)	P–N(2)–P′	98.5(1)
N(2)–P–N(3)	111.1(1)	P–N(3)–C(1)	123.3(2)
N(2)–P–N(2′)	81.5(1)	P–N(3)–C(2)	121.3(3)
P–N(1)–C(11)	128.7(2)	C(1)–N(3)–C(2)	115.1(3)

The structure of compound (**2**) is shown in the Figure and selected bond lengths and angles are given in Table 1. The molecule is centrosymmetric. The four-membered N_2P_2 ring is virtually planar. The phenyl rings attached to the ring nitrogen atoms are coplanar with the N_2P_2 ring (dihedral angle 1.0°). The ring nitrogen atoms and the nitrogen atoms of the dimethylamino groups are trigonal planar, with the angles around each nitrogen atom summing to *ca.* 360°. The phosphorus atoms adopt a distorted tetrahedral geometry. Within the N_2P_2 ring, the P–N distances and P–N–P and N–P–N bond angles are close to those observed for cyclodiphosphazanes with exocyclic P=S bonds.[5]

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† 2,4-Bis(dimethylamino)-1,3-diphenyl-2,4-bis(phenylimino)-1,3,2λ^5,4λ^5-diazadiphosphetidine.

‡ A preliminary account of this work was presented at the 5th International Symposium on Inorganic Ring Systems, Amherst, Massachusetts, August 1988.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

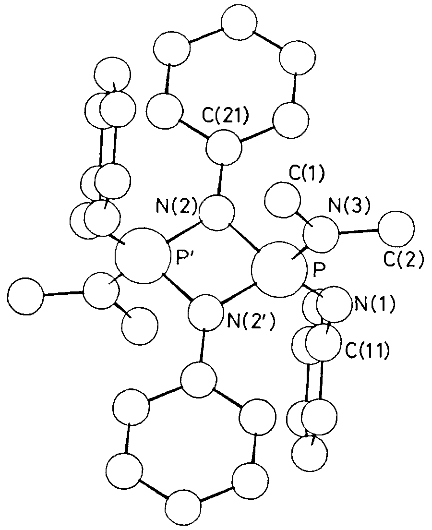
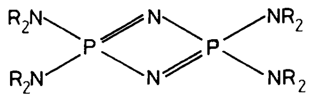


Figure. Perspective view of the molecule $[(PhN)P(NMe_2)(NPh)]_2$, (**2**) (H atoms omitted)

It is worthwhile to compare the structural features of compound (**2**) with those of (**3**), the first stable cyclodiphosphazene for which the *X*-ray structure is known.[10] Both compounds contain phosphorus centres bonded to four nitrogen atoms. In the case of (**3**) the N_2P_2 ring is planar and the exocyclic nitrogen atoms are trigonal planar. All endo- and exo-cyclic P–N bond lengths are equal (1.650 Å) and it is suggested that unsaturation is evenly delocalised over the ring skeleton and the exocyclic nitrogen atoms. By contrast, three different P–N bond lengths are observed for the bis(imino) derivative (**2**). The endocyclic P–N bonds are the longest (1.700 Å) presumably as a result of the competition for the lone pair of electrons on the nitrogen by the aryl group; the exocyclic P–NMe_2 bonds are shorter (1.625 Å) signifying appreciable multiple-bond character. The exocyclic P=N bonds are the shortest (1.518 Å) and this value indicates that the exocyclic P=N bond is not delocalised with the N_2P_2 ring system. The effect of multiple bonding within the N_2P_2 ring in (**3**) is also reflected in the considerable widening of the endocyclic angle at phosphorus (N–P–N) and a corresponding decrease in the P–N–P angle (95.0 and 85.0° respectively) compared to the values for compound (**2**) (81.5 and 98.5° respectively). Such a trend (*viz.* increase in the ring N–P–N angle and decrease in P–N–P angle with strengthening of skeletal π bonding) is well documented for cyclotri- and cyclotetra-phosphazene derivatives, $(NPX_2)_n$ (n = 3 or 4).[12]



(**3**) R = Pr^i

Experimental

The i.r. spectrum (4 000—400 cm^{-1}) was recorded using a Carl-Zeiss UR-10 spectrometer, the ^1H n.m.r. spectrum on a Bruker FT-270 (270 MHz) spectrometer with $SiMe_4$ as the internal standard, and the ^{31}P n.m.r. spectrum at 32.2 MHz on a Varian FT-80A spectrometer, chemical shifts downfield from the external standard, 85% H_3PO_4, being assigned positive values. Elemental analyses were performed at the City University, London, by Dr. S. A. Matlin. Phenyl azide[13] and *trans*-$[(PhN)P(NMe_2)]_2$[11] were prepared by literature methods.

Table 2. Atomic positional parameters for $[(PhN)P(NMe_2)(NPh)]_2$, (**2**), with estimated standard deviations in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
P	0.571 08(6)	0.623 01(9)	0.978 79(4)
N(1)	0.528 1(2)	0.748 4(3)	0.923 5(1)
N(2)	0.553 9(2)	0.429 4(2)	0.958 7(1)
N(3)	0.747 6(2)	0.663 2(2)	1.015 8(1)
C(1)	0.848 6(4)	0.782 8(5)	0.990 1(3)
C(2)	0.819 5(5)	0.569 5(8)	1.073 7(3)
C(11)	0.387 1(3)	0.763 6(3)	0.878 1(1)
C(12)	0.265 5(3)	0.860 5(4)	0.897 1(1)
C(13)	0.127 6(3)	0.876 5(5)	0.852 6(2)
C(14)	0.110 1(4)	0.800 4(5)	0.789 2(2)
C(15)	0.231 1(5)	0.706 1(5)	0.769 3(2)
C(16)	0.368 9(3)	0.689 5(4)	0.812 8(1)
C(21)	0.628 8(2)	0.337 8(3)	0.908 6(1)
C(22)	0.594 6(3)	0.180 9(3)	0.900 5(1)
C(23)	0.668 9(3)	0.092 2(4)	0.851 5(1)
C(24)	0.777 9(3)	0.160 2(3)	0.810 0(1)
C(25)	0.812 5(3)	0.316 3(4)	0.818 2(1)
C(26)	0.739 0(2)	0.406 4(3)	0.867 1(1)

Synthesis of $[(PhN)P(NMe_2)(NPh)]_2$ (**2**).—Phenyl azide (0.72 g, 6 mmol) was added to a solution of $[(PhN)P(NMe_2)]_2$ (**1**) (1.0 g, 3 mmol) in toluene (15 cm^3). After effervescence (caused by evolution of N_2) had ceased (*ca.* 10 min), the solution was heated under reflux for 12 h and filtered. The filtrate was cooled to obtain the required compound (0.95 g, 61%) as colourless crystals. Recrystallisation from dichloromethane gave well formed crystals suitable for *X*-ray structure determination, m.p. 186—194 °C (decomp.) (Found: C, 64.5; H, 6.3; N, 16.2. $C_{28}H_{32}N_6P_2$ requires C, 65.4; H, 6.2; N, 16.3%). I.r. spectrum (Nujol mull): 1 595s, 1 495s, 1 365s, 1 285s, 1 275s, 1 205w, 1 195w, 1 115s, 1 095m, 1 080w, 1 040w, 1 015s, 1 010s, 965s, 930s, 905w, 770m, 705w, 550w, 530w, and 480s cm^{-1}. N.m.r.: ^1H ($CDCl_3$), δ 2.65 (d with virtual coupling, J_{PH} = 11 Hz) and 6.70—7.50 (m); ^{31}P-{^1H} ($CHCl_3$), δ −23.6 (s) p.p.m.

Crystallographic Studies.—*Crystal data.* $C_{28}H_{32}N_6P_2$, M = 514, monoclinic, space group $P2_1/n$ (alternative $P2_1/c$, no. 14), a = 8.405(2), b = 8.536(1), c = 18.844(3) Å, β = 94.51(2)°, U = 1 347.8 $Å^3$, Z = 2, D_c = 1.268 g cm^{-3}, $F(000)$ = 544, λ = 0.709 26 Å, $\mu(Mo\text{-}K_\alpha)$ = 1.942 cm^{-1}, crystal size = 0.4 × 0.3 × 0.3 mm.

Data collection. An Enraf-Nonius CAD-4 four-circle diffractometer with graphite-monochromatised Mo-K_α radiation was used to measure the unit-cell dimensions and to collect the data. The unit-cell constants were obtained by least-squares analysis of the diffractometer setting angles of 25 well centred reflections with $20 \leqslant 2\theta \leqslant 28°$. The intensities of 3 213 reflections with $4 \leqslant 2\theta \leqslant 50°$ were recorded using ω—2θ scans. Of these, 2 364 reflections were unique and 1 424 had $I > 2\sigma(I)$. The intensities were reduced to a standard scale using routine procedures.[14] Corrections for Lorentz and polarisation factors were applied, but not for absorption. Scattering factors for neutral atoms were taken from ref. 15 and were corrected for the real and imaginary parts of anomalous dispersion.

Structure solution and refinement. The structure was solved by direct methods (MULTAN 80)[16] from which phosphorus, nitrogen, and most carbon atom positions were obtained. The remaining non-hydrogen-atom positions were determined from a Fourier difference synthesis. Refinement was carried out by using the SHELX 76 system.[17] The structure was refined initially by a full-matrix least-squares procedure with independent isotropic thermal parameters for the heavy atoms. Only the hydrogen atoms of the phenyl rings could be seen in a Fourier difference synthesis, and all hydrogen atoms were placed in their geometrically correct positions (C–H 1.08 Å). The hydrogen atoms were then allowed to refine freely with satisfactory results. The final refinements were with anisotropic thermal parameters for the non-hydrogen atoms and isotropic parameters for the hydrogen atoms and the positions of all atoms free to refine. A three-block-matrix least-squares method was employed minimising $\Sigma w \Delta F^2$ where $w^{-1} = \sigma^2|F_o| + 0.001|F_o|^2$. The refinement converged at $R = 0.036$, $R' = 0.035$ for 1 413 unique observed reflections [$I > 2\sigma(I)$] and 229 least-squares parameters. Eleven reflections were omitted because of suspected extinction. The final difference maps were flat, without recognisable residual features. The final atomic positional parameters of the non-hydrogen atoms are given in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond distances and angles.

Acknowledgements

Thanks are due to the Council of Scientific and Industrial Research, New Delhi, India for a fellowship (to S. S. K.) and the International Organisation of Chemical Sciences in Development (IOCD) (City University, London) for elemental analyses.

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Received 12*th May* 1989; *Paper* 9/01997I