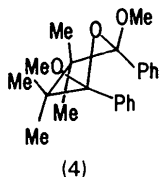


C—O—C angles observed in other less stable ozonides which are in the range 101.8 (2)–118.0 (5)° (Miura *et al.*, 1983; McCullough, Walkinshaw & Nojima, 1981). The average C—O(1) distance, 1.416 (2) Å, is within the range of values reported for similar systems, (Groth, 1969; McConnel & Stevens, 1973; Karban *et al.*, 1978; Grand & Cadet, 1978; Mullica *et al.*, 1979; Oliver *et al.*, 1979; Foss, Gardner, Kirschenheuter, Griffin & Stevens, 1986).

The C(1)—C(11) [1.486 (5) Å] and C(4)—C(5) [1.492 (6) Å] bonds are significantly shorter than the corresponding distances (Foss *et al.*, 1986) [1.518 (3) and 1.519 (3) Å, respectively] in (4). This probably results from the distortion of C(1) and C(4) away from ideal tetrahedral geometry owing to the bicyclic ring system, resulting in reduced steric interaction with the phenyl rings. The additional freedom in (4) owing to the absence of the peroxide bond allows a twist about the C(2)—C(3) bond to minimize nonbonded repulsion between methyl groups (Foss *et al.*, 1986).



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Structure of 2,4,4,8,8-Pentakis(dimethylamino)-9-methyl-6-methylamino-2,6-imino-2λ⁵,4λ⁵,6λ⁵,8λ⁵-cyclotetra(phosphazene) Monohydrate

BY T. STANLEY CAMERON, RUTH E. CORDES AND BEVERLY R. VINCENT

Department of Chemistry, Dalhousie University, Halifax, NS, Canada B3H 4J3

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Abstract. C₁₂H₃₇N₁₁P₄.H₂O, *M_r* = 477.4, triclinic, *P* $\bar{1}$, *a* = 15.181 (4), *b* = 9.388 (2), *c* = 18.103 (5) Å, α = 86.97 (3), β = 101.84 (3), γ = 99.75 (3)°, *Z* = 4, *D_x* = 1.274 (1) g cm⁻³, λ (Cu K α_1) = 1.54056 Å, μ = 29.91 cm⁻¹, *F*(000) = 1024, *T* = 298 K. *R* = 0.037 based on 3558 observed reflections. There are two non-equivalent molecules of a bicyclic phosphazene

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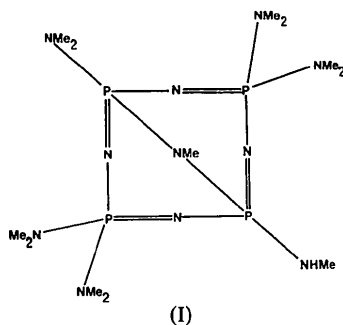
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each with a methylimino group bridging two P atoms. The two P—N bond lengths in the bridge are non-equivalent and are longer than any other P—N bonds in the compound. There are two water molecules in the asymmetric unit which are hydrogen-bonded together and these in turn bind the two non-equivalent phosphazene molecules together.

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Introduction. The first bicyclic phosphazene structure to be reported was $N_4P_4(NMe_2)_5(NH_2)(NEt)$ (Cameron & Mannan, 1977). The only other reported example is $N_4P_4(NHMe)_6(NMe)$ (Cameron, Cordes & Jackman, 1979). In both of these compounds, a relationship was observed between the P–N bond lengths at the exocyclic N atoms and the sum of the interbond angles about the N atom. The present structure (I) has been determined in order to see whether this relationship can be extended and to see whether there is a significant difference in the lengths of the P–N bridging bonds with a different substitution pattern at the P atoms.



Experimental. Crystals provided by S. S. Krishnamurthy, Indian Institute of Science, Bangalore, India. Picker FACS-1 four-circle diffractometer used to measure unit-cell dimensions, refined from circle angles of 12 general reflections with Bragg angle in range 70–75°, and to collect intensities of 4664 reflections with $4 < \theta < 60^\circ$ using an ω - 2θ scan. Reflections collected had $-10 \leq h \leq 10$, $-17 \leq k \leq 17$ and $0 \leq l \leq 20$. Three standard reflections, 060, 0,0,11 and $6\bar{1}1$, measured periodically; intensity variation less than 3%. Of reflections collected, 3558 had $I > 3\sigma(I)$. Intensities reduced to a standard scale using routine procedures (Cameron & Cordes, 1979). Corrections for Lorentz and polarization factors applied, but no corrections made for absorption or extinction. Scattering factors for neutral atoms those recorded in *International Tables for X-ray Crystallography* (1974) and corrected for the real part of the anomalous-dispersion effect.

Structure solved by a multi-solution application of the tangent formula (Karle & Hauptman, 1958) using *SHELX76* (Sheldrick, 1976). The *E* map from the solution with the lowest Karle *R* factor clearly showed the positions of all P, N and C atoms. Structure refined on *F*, initially by a large-block least-squares procedure with isotropic temperature factors on heavy atoms. H-atom positions determined from difference Fourier synthesis carried out at an advanced stage of the refinement, all C–H and N–H distances appropriately constrained to ensure convergence (C–H bonds to

1.08 Å and N–H bonds to 1.02 Å), and methyl groups refined as rigid groups rotationally adjustable about the N–C axes. There was insufficient evidence to locate water H-atom positions with confidence.

Final refinements with anisotropic temperature factors on non-H atoms and a single overall isotropic temperature factor for H atoms in each of the two discrete molecules in the asymmetric unit. These were two-block-matrix refinements, with all parameters for each molecule being refined in one block. Sigma weighting scheme [$w\Delta F^2 = \min.$; $w^{-1} = \sigma(|F_o|)$] implemented in these final cycles, performed using *CRYSTALS* (Carruthers, 1979). Refinement converged at $R = 0.037$, $wR = 0.039$ for 513 least-squares parameters. Ratios of least-squares shifts to e.s.d.'s less than 0.15 for all parameters after last cycle of refinement. Final difference Fourier map revealed no peaks larger than 0.23 e \AA^{-3} , average residual electron density at atomic sites $0.14 (20) \text{ e \AA}^{-3}$.

The final atomic coordinates are given in Table 1.* The interatomic distances and interbond angles for the two molecules of (I) are given in Table 2. Fig. 1 is a stereoscopic view of one molecule of (I), and Fig. 2 shows the packing in the unit cell.

Discussion. There are two non-equivalent phosphazene molecules and two water molecules per asymmetric unit. Molecule 1 and molecule 2 are bonded together by two moderately strong hydrogen bonds [N(6)–H(100)···N(21), H(100)···N(21): 2.08 (1) Å, angle: 137 (3)°; and N(26)–H(101)···N(1), H(101)···N(1): 2.18 (1) Å, angle: 169 (3)°]. O(1) and O(2) of the water molecules are hydrogen-bonded to each other [O···O, 2.67 (1) Å]. O(1) also appears to be hydrogen-bonded to both N(4) [O···N, 3.05 (1) Å] and N(22,*x*–1) [O···N, 2.98 (1) Å]. The next-closest contacts are considerably longer than this; they are from O(1) to N(9) [O···N, 3.40 (1) Å] and O(2) to N(27,*x*–1) [O···N, 3.44 (1) Å]. Because the H atoms of the water molecules could not be located, the exact hydrogen-bonding arrangement is uncertain, but there appear to be chains of hydrogen-bonded molecules along *c*.

The phosphazene consists of an eight-membered ring, (PN)₄, with the first and third P atoms in the ring being bridged by a methylimino group. One of the bridged P atoms has an NHMe substituent, while the other is substituted by a dimethylamino group. The second and fourth P atoms are both disubstituted with

* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, torsion angles and references pertaining to the Cambridge Structural Database have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42909 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional* ($\times 10^4$) and *thermal parameters* (\AA^2)

Mod(<i>U</i>) is defined as $(U_{11}U_{22}U_{33})^{1/3}$.				
	<i>x</i>	<i>y</i>	<i>z</i>	Mod(<i>U</i>)
P(1)	7001 (1)	2475 (1)	7641 (1)	0.04056
P(2)	6472 (1)	4795 (2)	6725 (1)	0.04497
P(3)	5284 (1)	2176 (2)	6716 (1)	0.04481
P(4)	5436 (1)	2098 (2)	8280 (1)	0.04724
N(1)	7246 (2)	4025 (4)	7266 (2)	0.04308
N(2)	5535 (3)	3753 (5)	6398 (2)	0.05266
N(3)	6270 (2)	1430 (4)	6960 (2)	0.04262
N(4)	4839 (3)	1956 (5)	7449 (2)	0.05397
N(5)	6520 (3)	2316 (5)	8344 (2)	0.04766
N(6)	7961 (3)	1847 (5)	7871 (2)	0.04808
N(7)	6332 (3)	6167 (5)	7192 (2)	0.05668
N(8)	6820 (3)	5643 (6)	5982 (3)	0.06717
N(9)	4599 (3)	1241 (5)	6035 (3)	0.05568
N(10)	5139 (3)	3411 (5)	8685 (3)	0.06285
N(11)	5185 (3)	673 (5)	8822 (3)	0.06056
C(3)	6670 (4)	1149 (6)	6313 (3)	0.06120
C(6)	8132 (4)	698 (7)	8399 (4)	0.07749
C(71)	5668 (5)	7081 (7)	6841 (4)	0.08141
C(72)	6622 (4)	6334 (7)	7994 (3)	0.07071
C(81)	7622 (4)	6764 (9)	6122 (4)	0.09138
C(82)	6714 (6)	4904 (9)	5289 (4)	0.11016
C(91)	4175 (4)	-234 (7)	6186 (4)	0.06860
C(92)	4338 (6)	1767 (8)	5286 (4)	0.08803
C(101)	5547 (5)	3721 (8)	9465 (4)	0.09489
C(102)	4414 (5)	4192 (8)	8355 (5)	0.09788
C(111)	4236 (4)	321 (8)	8944 (4)	0.08852
C(112)	5555 (5)	-597 (7)	8721 (4)	0.08919
O(1)	2801 (4)	1666 (10)	6804 (5)	0.17358
P(21)	10030 (1)	4669 (2)	7815 (1)	0.04440
P(22)	10366 (1)	2679 (2)	6863 (1)	0.05257
P(23)	11777 (1)	4825 (2)	7551 (1)	0.04668
P(24)	11501 (1)	4444 (2)	9017 (1)	0.05347
N(21)	9689 (3)	3287 (5)	7300 (3)	0.05145
N(22)	11424 (3)	3401 (5)	7071 (3)	0.05504
N(23)	10871 (3)	5751 (4)	7456 (2)	0.04584
N(24)	12156 (3)	4688 (5)	8420 (3)	0.05589
N(25)	10431 (3)	4435 (5)	8674 (2)	0.05717
N(26)	9175 (3)	5556 (5)	7708 (3)	0.05214
N(27)	10353 (3)	932 (5)	6983 (3)	0.06773
N(28)	9952 (3)	2836 (6)	5952 (3)	0.07174
N(29)	12581 (3)	5799 (5)	7174 (3)	0.06025
N(210)	11584 (3)	2917 (6)	9477 (3)	0.07620
N(211)	11918 (3)	5687 (6)	9666 (3)	0.06922
C(23)	10595 (4)	6373 (6)	6696 (3)	0.06380
C(26)	9215 (4)	6767 (6)	8178 (4)	0.07118
C(271)	10811 (6)	419 (8)	7699 (4)	0.09507
C(272)	9472 (5)	-19 (7)	6690 (5)	0.08532
C(281)	9062 (5)	3208 (9)	5628 (4)	0.08974
C(282)	10457 (6)	2440 (10)	5418 (4)	0.10494
C(291)	13097 (4)	7102 (8)	7542 (4)	0.08101
C(292)	12659 (5)	5694 (9)	6394 (4)	0.09222
C(21)	10831 (5)	1884 (8)	9650 (4)	0.09330
C(22)	12482 (5)	2577 (11)	9822 (5)	0.11878
C(211)	12103 (6)	7187 (9)	9415 (5)	0.10581
C(212)	11509 (6)	5661 (10)	10325 (4)	0.11469
O(2)	1686 (7)	-355 (10)	5927 (7)	0.22612

dimethylamino groups. Each ring is V-shaped, with each of the two halves, [P(1), N(1), P(2), N(2), P(3)] and [P(1), N(5), P(4), N(4), P(3)], being essentially planar. The two planes are inclined at an angle of $115(1)^\circ$, and the planes make angles of $119(1)$ and $126(1)^\circ$ with the plane defined by the methylimino bridge, P(1), N(3), P(3). This is similar to the geometry of $N_4P_4(NHMe)_6(NMe)$ with an angle of 122.4° between the two halves of the molecule, and angles of 122.3 and 115.2° to the bridge. However, this is in contrast with the geometry of $N_4P_4(NMe)_5(NHET)(NEt)$, which showed a 120° angle between the two planes, and angles of 142.5 and 96.2° respectively between each of the two planes and the plane of the bridge.

The greatest separation between two P atoms in each molecule is that between the two non-bridged P atoms, and is $4.228(1)$ Å in molecule 1 and $4.065(1)$ Å in molecule 2. All other P...P distances in both molecules are in the range $2.766(1)$ to $2.812(1)$ Å with a mean of $2.790(6)$ Å.

The longest P—N bonds in the molecule are those involving the bridging group. These distances, at $1.706(4)$ and $1.725(4)$ Å for molecule 1 and $1.708(4)$ and $1.723(4)$ Å for molecule 2, are about 0.1 Å longer than other P—N bonds within the ring, and 0.05 Å longer than the exocyclic P—N bonds. The two previous bicyclic phosphazenes reported had bridging P—N bond lengths of $1.723(6)$, $1.709(6)$, $1.76(1)$ and $1.73(1)$ Å. All other cyclic P—N bond lengths in (I) fall in the range $1.581(4)$ to $1.615(4)$ Å, while the exocyclic P—N bonds are all between $1.628(4)$ and $1.656(4)$ Å.

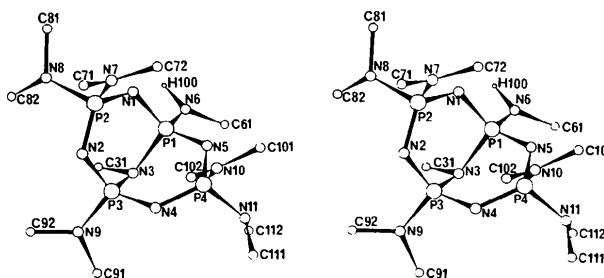


Fig. 1. A stereoscopic view of molecule 1. Molecule 2 is similar.

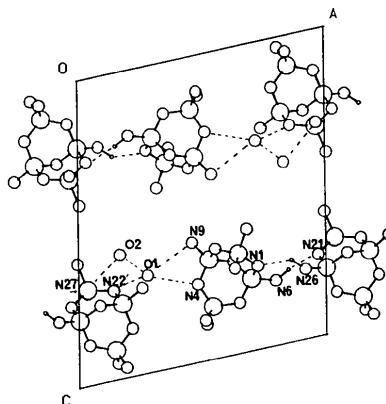


Fig. 2. Packing diagram viewed down the *b* axis. Hydrogen bonding is indicated by dashed lines. Methyl groups have been removed for clarity.

The C—N lengths in the methylamino and dimethylamino groups range between 1.420 (8) and 1.480 (6) Å with a mean value of 1.45 (2) Å.

From Table 2 it can be seen that the two unique molecules of (I) are very similar in geometry, with all

bonds agreeing to within 0.015 Å, except for P(3)—N(4) and P(23)—N(24), which differ by 0.031 Å. This can be explained by the involvement of both N(4) and N(9), the latter bonded to P(3), in hydrogen bonding to water molecules.

Cameron & Mannan (1977) obtained a straight line from a plot of exocyclic P—N bond lengths against the sum of the interbond angles about the N atom. A plot of these parameters for all fully reported dialkylamino-substituted phosphazenes yielded a scatter plot, Fig. 3, of some 82 points from 14 different structures (Cambridge Structural Database, 1984; a full list of references has been deposited). Exocyclic P—N bond lengths in all structures ranged between 1.61 (1) and 1.72 (1) Å, with a weighted mean of 1.644 (12) Å (weights based on the e.s.d. of the length) and the sum of interbond angles ranged between 344.5 (4) and the maximum value of 360° with a mean value of 354 (4)°. The plot showed no clear relationship between these parameters. Also included in this plot is the point corresponding to potassium phosphoramidate (Cameron, Chan & Chute, 1980), which corresponds to an 'ideal' P—N single bond. There are three other structures included where the two C atoms bonded to the N atom in question are bonded to each other, in the

Table 2. *Interatomic distances (Å) and angles (°)*

P(1)—N(1)	1.591 (4)	P(21)—N(21)	1.588 (4)
P(1)—N(3)	1.706 (4)	P(21)—N(23)	1.708 (4)
P(1)—N(5)	1.581 (4)	P(21)—N(25)	1.568 (4)
P(1)—N(6)	1.631 (4)	P(21)—N(26)	1.631 (4)
P(2)—N(1)	1.613 (4)	P(22)—N(21)	1.609 (4)
P(2)—N(2)	1.605 (4)	P(22)—N(22)	1.610 (4)
P(2)—N(7)	1.643 (4)	P(22)—N(27)	1.640 (4)
P(2)—N(8)	1.661 (4)	P(22)—N(28)	1.648 (4)
P(3)—N(2)	1.574 (2)	P(23)—N(22)	1.587 (4)
P(3)—N(3)	1.725 (4)	P(23)—N(23)	1.723 (4)
P(3)—N(4)	1.598 (4)	P(23)—N(24)	1.567 (4)
P(3)—N(9)	1.628 (4)	P(23)—N(29)	1.640 (4)
P(4)—N(4)	1.588 (4)	P(24)—N(24)	1.596 (4)
P(4)—N(5)	1.604 (4)	P(24)—N(25)	1.614 (4)
P(4)—N(10)	1.637 (4)	P(24)—N(210)	1.630 (4)
P(4)—N(11)	1.655 (4)	P(24)—N(211)	1.653 (4)
N(3)—C(3)	1.480 (6)	N(23)—C(23)	1.473 (6)
N(6)—C(6)	1.424 (6)	N(26)—C(26)	1.441 (6)
N(7)—C(71)	1.459 (6)	N(27)—C(271)	1.440 (8)
N(7)—C(72)	1.437 (6)	N(27)—C(272)	1.491 (8)
N(8)—C(81)	1.457 (8)	N(28)—C(281)	1.451 (8)
N(8)—C(82)	1.433 (8)	N(28)—C(282)	1.449 (8)
N(9)—C(91)	1.462 (6)	N(29)—C(291)	1.450 (6)
N(9)—C(92)	1.419 (8)	N(29)—C(292)	1.451 (6)
N(10)—C(101)	1.444 (8)	N(210)—C(21)	1.444 (8)
N(10)—C(102)	1.436 (8)	N(210)—C(22)	1.459 (8)
N(11)—C(111)	1.482 (6)	N(211)—C(211)	1.456 (9)
N(11)—C(112)	1.436 (8)	N(211)—C(212)	1.451 (8)
N(1)—P(1)—N(3)	106.9 (2)	N(21)—P(21)—N(23)	107.9 (2)
N(1)—P(1)—N(5)	120.0 (2)	N(21)—P(21)—N(25)	118.3 (3)
N(1)—P(1)—N(6)	105.6 (2)	N(21)—P(21)—N(26)	106.5 (2)
N(3)—P(1)—N(5)	105.3 (2)	N(23)—P(21)—N(25)	106.2 (2)
N(3)—P(1)—N(6)	109.8 (2)	N(23)—P(21)—N(26)	106.8 (2)
N(5)—P(1)—N(6)	109.1 (2)	N(25)—P(21)—N(26)	110.6 (2)
N(1)—P(2)—N(2)	115.7 (2)	N(21)—P(22)—N(22)	116.2 (2)
N(1)—P(2)—N(7)	106.7 (2)	N(21)—P(22)—N(27)	113.2 (2)
N(1)—P(2)—N(8)	113.2 (3)	N(21)—P(22)—N(28)	107.1 (3)
N(2)—P(2)—N(7)	113.4 (2)	N(22)—P(22)—N(27)	105.6 (2)
N(2)—P(2)—N(8)	106.1 (3)	N(22)—P(22)—N(28)	111.3 (3)
N(7)—P(2)—N(8)	100.9 (2)	N(27)—P(22)—N(28)	102.7 (3)
N(2)—P(3)—N(3)	108.3 (2)	N(22)—P(23)—N(23)	107.0 (2)
N(2)—P(3)—N(4)	118.9 (3)	N(22)—P(23)—N(24)	119.2 (3)
N(2)—P(3)—N(9)	107.4 (2)	N(22)—P(23)—N(29)	107.3 (2)
N(3)—P(3)—N(4)	104.9 (2)	N(23)—P(23)—N(24)	106.1 (2)
N(3)—P(3)—N(9)	108.5 (2)	N(23)—P(23)—N(29)	109.1 (2)
N(4)—P(3)—N(9)	108.5 (2)	N(24)—P(23)—N(29)	107.8 (2)
N(4)—P(4)—N(5)	115.9 (2)	N(24)—P(24)—N(25)	115.8 (2)
N(4)—P(4)—N(10)	107.6 (3)	N(24)—P(24)—N(210)	110.6 (3)
N(4)—P(4)—N(11)	112.4 (3)	N(24)—P(24)—N(211)	106.4 (3)
N(5)—P(4)—N(10)	111.3 (2)	N(25)—P(24)—N(210)	106.9 (3)
N(5)—P(4)—N(11)	105.8 (2)	N(25)—P(24)—N(211)	112.5 (3)
N(10)—P(4)—N(11)	103.2 (3)	N(210)—P(24)—N(211)	104.2 (3)
P(1)—N(1)—P(2)	121.3 (2)	P(21)—N(21)—P(22)	121.0 (3)
P(2)—N(2)—P(3)	122.8 (3)	P(22)—N(22)—P(23)	123.2 (3)
P(1)—N(3)—P(3)	107.8 (2)	P(21)—N(23)—P(23)	107.6 (2)
P(1)—N(3)—C(3)	114.5 (3)	P(21)—N(23)—C(23)	116.2 (3)
P(3)—N(3)—C(3)	114.5 (3)	P(23)—N(23)—C(23)	114.3 (3)
P(3)—N(4)—P(4)	122.4 (3)	P(23)—N(24)—P(24)	122.0 (3)
P(1)—N(5)—P(4)	124.0 (3)	P(21)—N(25)—P(24)	123.9 (3)
P(1)—N(6)—C(6)	125.3 (4)	P(21)—N(26)—C(26)	120.7 (4)
P(2)—N(7)—C(71)	119.4 (4)	P(22)—N(27)—C(271)	117.9 (5)
P(2)—N(7)—C(72)	124.5 (4)	P(22)—N(27)—C(272)	116.6 (4)
C(71)—N(7)—C(72)	113.9 (5)	C(271)—N(27)—C(272)	121.1 (6)
P(2)—N(8)—C(81)	117.7 (4)	P(22)—N(28)—C(281)	125.0 (5)
P(2)—N(8)—C(82)	120.9 (5)	P(22)—N(28)—C(282)	119.0 (5)
C(81)—N(8)—C(82)	113.4 (6)	C(281)—N(28)—C(282)	115.7 (6)
P(3)—N(9)—C(91)	119.8 (4)	P(23)—N(29)—C(291)	119.7 (4)
P(3)—N(9)—C(92)	124.8 (4)	P(23)—N(29)—C(292)	123.9 (4)
C(91)—N(9)—C(92)	115.4 (5)	C(291)—N(29)—C(292)	114.3 (5)
P(4)—N(10)—C(101)	119.1 (4)	P(24)—N(210)—C(21)	125.6 (5)
P(4)—N(10)—C(102)	125.0 (5)	P(24)—N(210)—C(22)	119.7 (5)
C(101)—N(10)—C(102)	115.5 (5)	C(21)—N(210)—C(22)	114.4 (6)
P(4)—N(11)—C(111)	117.6 (4)	P(24)—N(211)—C(211)	118.0 (5)
P(4)—N(11)—C(112)	116.9 (4)	P(24)—N(211)—C(212)	119.3 (5)
C(111)—N(11)—C(112)	112.2 (5)	C(211)—N(211)—C(212)	107.6 (6)

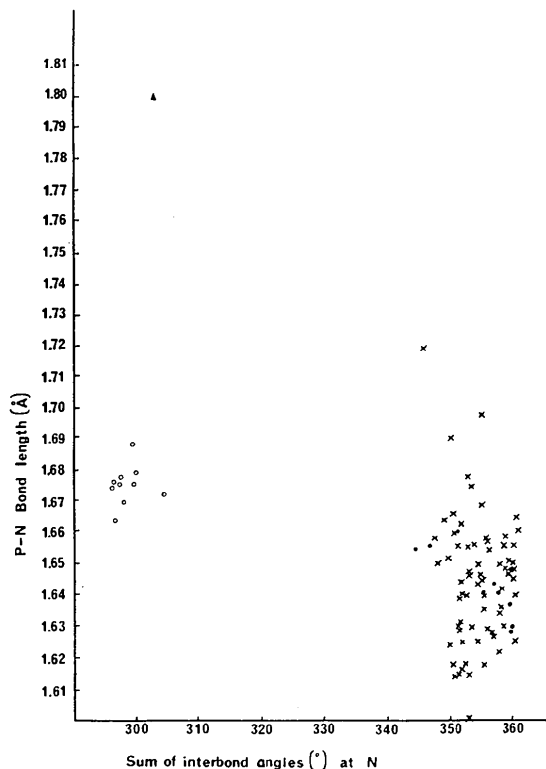


Fig. 3. A plot of the sum of the interbond angles at the exocyclic N atoms against the corresponding P—N bond length; ● the title compound, ▲ Cameron *et al.* (1980), × Cambridge Structural Database (1984), ○ aziridinyl cyclo(phosphazenes).

form of an aziridinyl group, placing constraints on the sum of the angles about N. Clearly these compounds form a separate series from the remaining structures.

The relationship, which has been observed previously for select structures, between the P—N bond length and the sum of the interbond angles at N is apparently not a general trend, and no such relationship can be derived for 17 compounds reported to date.

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Structure of 3-Hydroxy-6-(4'-methyl)phenylazopyridine*

BY T. SIVA RAMA KRISHNA AND GAUTAM R. DESIRAJU†

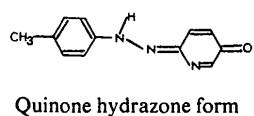
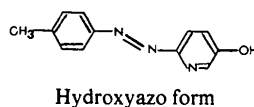
School of Chemistry, University of Hyderabad, PO Central University, Hyderabad – 500 134, India

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Abstract. C₁₂H₁₁N₃O, *M_r* = 213.24, orthorhombic, *P*2₁2₁2₁, *a* = 8.2537 (8), *b* = 9.3545 (6), *c* = 14.6981 (10) Å, *V* = 1134.8 (4) Å³, *Z* = 4, *D_m* = 1.22, *D_x* = 1.25 Mg m⁻³, *F*(000) = 448, λ(Cu Kα) = 1.54178 Å, μ(Cu Kα) = 5.93 mm⁻¹, *R* = 0.035, *wR* = 0.034 with 720 independent non-zero reflections. The molecule exists as the hydroxyazo tautomer, the angle between the phenyl and pyridyl rings is 26 (1)° and the hydroxyl group of one molecule is hydrogen-bonded to the heterocyclic N of the screw-related neighbour. This intermolecular hydrogen-bonding pattern is also a confirmation of the azo structure. The adoption of a non-centrosymmetric space group by the title compound is discussed.

Introduction. Several chemical and spectroscopic methods have been used to study the tautomerism of hydroxyazo compounds in solution (Zollinger, 1961; Morgan, 1961; Saeva, 1971). Generally, azophenols exist as the hydroxyazo tautomer while the quinone hydrazone form predominates for azonaphthols. Crystallographic results on such systems are, however, sparse (Pendergrass, Curtin & Paul, 1972; Guggenberger & Teufer, 1975; Kurahashi, 1976). Data on azopyridines are even more uncommon and this study follows from an earlier one (Desiraju, 1983) where the crystal structures of both azo and hydrazone forms of

2-amino-3-hydroxy-6-phenylazopyridine were reported. This paper is part of a systematic attempt to determine the effects of substituents on the stability of azopyridine tautomers in the solid state, especially in those cases where the solid-state behaviour differs from that in solution.



Experimental. Dark-red needles, prepared by diazonium coupling of *p*-toluidine with 3-hydroxypyridine and recrystallization from EtOH, *D_m* by flotation in CCl₄—benzene, data collected on an Enraf–Nonius CAD-4 diffractometer, lattice parameters from 25 high-angle reflections (matrix check reflections 254 and $\bar{3}\bar{4}\bar{1}$), systematic absences: *h*00, *h* = 2*n* + 1; 0*k*0, *k* = 2*n* + 1; 00*l*, *l* = 2*n* + 1, no absorption or extinction corrections applied, maximum sinθ/λ = 0.61 Å⁻¹, ranges of *h*, *k* and *l*, 0 to 10, 0 to 10 and 0 to 17, standards ($\bar{1}\bar{4}\bar{3}$ and $\bar{1}\bar{4}\bar{0}$) did not vary more than 4%, 1183 reflections measured, 717 unique non-zero reflections at

* IUPAC name: 5-hydroxypyridine-2-azo(4'-methylbenzene).

† To whom correspondence should be addressed.