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The Crystal Structure of an Unusual Bicyclic Phosphazene $N_4P_4(NMe_2)_5(NHEt)(NEt)$

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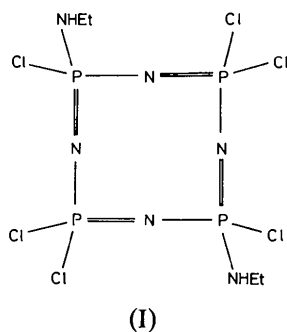
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The structure of the title compound has been determined by the heavy-atom method and refined by least squares to $R = 0.008$. $a = 10.81$, $b = 17.52$, $c = 28.48$ Å, $\beta = 94.8^\circ$, space group $C2/c$, 921 reflexions. The molecule is a bicyclic phosphazene with an ethylamine group bridging two P atoms. The exocyclic P–N length appears to be related to the deviation from coplanarity of the three atoms bonded to the N atom.

In an investigation into the reaction of the phosphazene (I) with an excess of Me_2NH an unusual crystalline product was obtained (Keat *et al.*, 1976). The structural formula of this product has been determined by X-ray crystallography (Cameron *et al.*, 1975).



Experimental

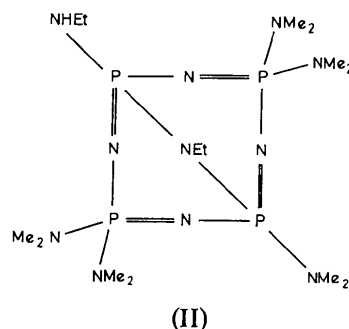
The crystals were provided by S. Krishnamurthy and A. C. Sau, Indian Institute of Science, Bangalore.

Crystal data

$C_{14}H_{41}N_{11}P_4$, $M_r = 463.3$, $a = 10.81$ (1), $b = 17.52$ (1), $c = 28.48$ (2) Å, $\beta = 94.8$ (2)°, $D_m = 1.21$, $Z = 8$, $D_c = 1.205$ g cm⁻³. Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å, $\mu = 26.6$ cm⁻¹; systematic extinctions: hkl $h + k = 2n + 1$, $h0l$ $l = 2n + 1$, space group $C2/c$.

The intensities of 921 reflexions were estimated from equi-inclination Weissenberg photographs (0–10, k , l) by the Harwell film-scanning service.

The positions of four P atoms were determined from an unsharpened Patterson function and the locations of the remaining non-hydrogen atoms found in the subsequent F_o synthesis.



The structure (II) was refined by full-matrix least squares, initially with isotropic temperature factors for all atoms when it converged with $R = 0.11$ and then, after a difference synthesis showed appreciable anisotropy of the P atoms, with anisotropic temperature factors on these four atoms only. The refinement ultimately converged at $R = 0.088$. Nearly all the H atoms present are in methyl groups and their locations are not precisely defined by molecular geometry. At no stage in the refinement was it possible to attribute positions with any authority to the H atoms. However, the most prominent peak in the difference synthesis calculated at $R = 0.088$ was in a reasonable position for the H atom of the NHet group. The sum of the interbond angles about the N atom of this group is included in Table 3 although the position of the H atom was never refined. Weights were given by $\omega = [F_o + 0.001(F_o)^2]^{-1}$.

All the calculations used Sheldrick's (1975) system*

* The system became available after the preliminary communication of this structure was published (Cameron *et al.*, 1975). The refinement has since been recalculated.

on the University of Ulster's ICL 1903A computer.*

Table 1 lists the atomic parameters. The scattering factors were those in *International Tables for X-ray Crystallography* (1974) and were corrected for dispersion. Table 2 gives the interatomic distances and interbond angles and Table 3 a list of the exocyclic P-N lengths with the sums of the interbond angles at the N atom. Fig. 1 shows a single molecule, and Fig. 2 the packing of the molecules in the unit cell. The diagrams were drawn by *STRPL* (Cameron, 1973).

Results and discussion

The crystal is constructed from isolated molecules (II) which pack together in planes parallel to (010) and (001). The cyclic P,N part is V-shaped with the bridging N(3) at the point at the bottom, and P(12) and P(4)

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32056 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Atomic parameters ($\times 10^4$)

	<i>x</i>	<i>y</i>	<i>z</i>	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
P(1)	1549 (5)	4362 (3)	5988 (2)	284	358	329	-20	0	86
P(2)	1942 (5)	5921 (4)	5955 (2)	344	380	356	84	28	78
P(3)	1224 (5)	5240 (4)	6787 (2)	249	575	227	-27	6	-14
P(4)	-809 (5)	4434 (4)	6340 (2)	237	585	284	-61	4	-23

Table I (cont.)

	<i>x</i>	<i>y</i>	<i>z</i>	U_{iso}
N(1)	1790 (14)	5704 (10)	5704 (6)	337
N(2)	1569 (15)	5971 (11)	6483 (7)	399
N(3)	2147 (14)	4539 (10)	6571 (6)	353
N(4)	-183 (15)	4937 (11)	6777 (6)	382
N(5)	159 (17)	4051 (11)	6032 (7)	425
N(6)	2398 (17)	3692 (12)	5753 (7)	495
N(7)	3413 (16)	6292 (11)	5951 (7)	466
N(8)	1127 (19)	6528 (13)	5616 (8)	663
N(9)	1627 (17)	5385 (11)	7367 (7)	485
N(10)	-1855 (16)	4981 (12)	6049 (7)	520
N(11)	-1685 (19)	3722 (13)	6511 (8)	646
C(1)	2000 (24)	2857 (17)	5759 (10)	666
C(2)	3623 (24)	3848 (16)	5565 (10)	610
C(3)	3914 (28)	6362 (19)	5488 (12)	880
C(4)	4399 (28)	6008 (20)	6319 (12)	889
C(5)	1035 (34)	7326 (23)	5752 (14)	1246
C(6)	314 (28)	6339 (19)	5188 (12)	969
C(7)	8054 (23)	5793 (16)	6083 (10)	653
C(8)	-2584 (27)	4689 (19)	5593 (12)	909
C(9)	-2895 (30)	3881 (21)	6735 (13)	981
C(10)	-1076 (26)	3037 (18)	6733 (11)	827
C(11)	2756 (27)	5902 (18)	7527 (12)	768
C(12)	2144 (46)	6633 (30)	7595 (19)	1719
C(13)	2338 (19)	3837 (13)	6867 (8)	404
C(14)	3723 (25)	3680 (16)	6986 (10)	660
H(1)	896	5381	7522	

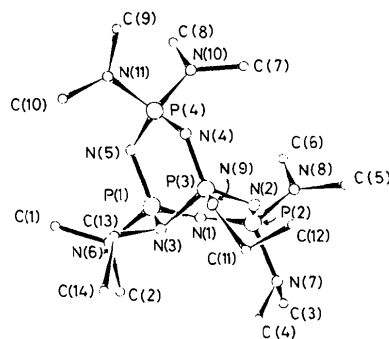


Fig. 1. The molecule projected perpendicular to *a*.

at the top. These two atoms are 4.06 Å apart while all other non-bonded P—P distances are in the range 2.77–2.81 Å. The portions of the rings P(3)—N(2)—P(2)—N(1)—P(1) and P(3)—N(4)—P(4)—N(5)—P(1) are each practically coplanar. The least-squares best planes through these two groups are inclined at 121.2°, and make angles of 142.5 and 96.2° respectively with the plane through atoms P(1)—N(3)—P(3). Within the cyclic fragment there is a wide variation in P—N lengths, with those at the bridging N atom 0.1 Å or more longer than the others. With the exception of the

bridge, the cyclic P—N lengths vary between 1.57 and 1.63 Å, which is within the range of accepted values for cyclic phosphazenes (Corbridge, 1974). The lengths give some support to the suggestion (De Decker & MacGillavry, 1941) that the π system in cyclic phosphazenes is constructed from three-centre bonds with discontinuities at each P atom, since within the rings two P—N bonds at all the N atoms are equal within experimental error (mean e.s.d. 0.013 Å). The small differences between the pairs of bond lengths [excluding those at N(3)] are probably due to steric and crystal packing requirements. The longer P—N lengths at the bridge are almost certainly not caused by a structural requirement to keep P(1) and P(3) widely separated since the non-bonded P(1)···P(3) distance of 2.79 Å is the second shortest in the structure. The longer lengths reflect the pyramidal nature of N(3) which is 0.47 Å from the plane of the three atoms bonded to it, the sum of the interbond angles being 336.8°. If the sum of the interbond angles at each of the N atoms with three substituents in this structure is plotted against the P—N length (Table 3), a straight line is obtained (Fig. 3). The only other phosphazenes containing several NMe₂ groups to be reported in full are P₃N₃(NMe₂)₆ (Rettig & Trotter, 1973) and P₄N₄(NMe₂)₈ (Bullen, 1962). The exocyclic P—N bonds in the trimer fall into two types. For four of them the sum of the interbond angles at the N atoms are in the range 348–352° (mean 350°) with a mean P—N length of 1.654 (2) Å; for the other two the sum of interbond angles is within a degree of 360° with a corresponding mean bond length of 1.648 (2) Å. The mean values from these two types of group are included in Fig. 3. The tetramer has fourfold symmetry and so there are just two unique NMe₂ groups (Bullen, 1962). The sums of the interbond angles at these N atoms are also plotted with the corresponding P—N lengths in Fig. 3. If this line is extended to the sum of interbond angles for

Table 2. *Interatomic distances and interbond angles*

P(1)—N(1)	1.57 (1) Å	N(1)—P(1)—N(3)	106.1 (3)°
P(1)—N(3)	1.76 (1)	N(1)—P(1)—N(5)	121.2 (4)
P(1)—N(5)	1.61 (1)	N(1)—P(1)—N(6)	104.8 (3)
P(1)—N(6)	1.66 (1)	N(3)—P(1)—N(5)	105.0 (3)
P(2)—N(1)	1.60 (1)	N(3)—P(1)—N(6)	109.4 (3)
P(2)—N(2)	1.59 (1)	N(5)—P(1)—N(6)	110.0 (3)
P(2)—N(7)	1.72 (1)	N(1)—P(2)—N(2)	116.5 (4)
P(2)—N(8)	1.64 (1)	N(1)—P(2)—N(7)	113.3 (4)
P(3)—N(2)	1.61 (1)	N(1)—P(2)—N(8)	106.7 (4)
P(3)—N(3)	1.73 (1)	N(2)—P(2)—N(7)	107.2 (4)
P(3)—N(4)	1.61 (1)	N(2)—P(2)—N(8)	110.7 (4)
P(3)—N(9)	1.69 (1)	N(7)—P(2)—N(8)	101.7 (3)
P(4)—N(4)	1.63 (1)	N(2)—P(3)—N(3)	102.1 (3)
P(4)—N(5)	1.57 (1)	N(2)—P(3)—N(4)	120.9 (4)
P(4)—N(10)	1.65 (1)	N(2)—P(3)—N(9)	110.7 (3)
P(4)—N(11)	1.66 (1)	N(3)—P(3)—N(4)	109.4 (4)
N(3)—C(13)	1.50 (2)	N(3)—P(3)—N(9)	110.2 (3)
N(6)—C(1)	1.53 (2)	N(4)—P(3)—N(9)	103.5 (4)
N(6)—C(2)	1.50 (2)	N(4)—P(4)—N(5)	113.9 (4)
N(7)—C(3)	1.47 (3)	N(4)—P(4)—N(10)	107.1 (4)
N(7)—C(4)	1.52 (3)	N(4)—P(4)—N(11)	113.1 (4)
N(8)—C(5)	1.46 (3)	N(5)—P(4)—N(10)	115.4 (4)
N(8)—C(6)	1.48 (3)	N(5)—P(4)—N(11)	105.4 (4)
N(9)—C(11)	1.56 (3)	N(10)—P(4)—N(11)	101.5 (4)
N(10)—C(7)	1.43 (2)	P(1)—N(1)—P(2)	121.8 (8)
N(10)—C(8)	1.55 (4)	P(1)—N(2)—P(3)	123.6 (10)
N(11)—C(9)	1.53 (3)	P(1)—N(3)—P(3)	106.5 (7)
N(11)—C(10)	1.49 (3)	P(1)—N(3)—C(13)	114.2 (8)
C(11)—C(12)	1.46 (4)	P(3)—N(3)—C(13)	116.1 (8)
C(13)—C(14)	1.53 (2)	P(3)—N(4)—P(4)	121.7 (9)
N(9)—H(1)	0.94	P(1)—N(5)—P(4)	124.6 (10)
		P(1)—N(6)—C(1)	120.3 (10)
		P(1)—N(6)—C(2)	123.4 (10)
		C(1)—N(6)—C(2)	116.0 (11)
		P(2)—N(7)—C(3)	116.6 (9)
		P(2)—N(7)—C(4)	118.0 (9)
		C(3)—N(7)—C(4)	110.9 (10)
		P(2)—N(8)—C(5)	120.7 (11)
		P(2)—N(8)—C(6)	126.3 (12)
		C(5)—N(8)—C(6)	112.7 (12)
		P(3)—N(9)—C(12)	120.5 (9)
		P(3)—N(9)—H(1)	107.5
		C(11)—N(9)—H(1)	122.4
		P(4)—N(10)—C(7)	126.3 (10)
		P(4)—N(10)—C(8)	120.6 (10)
		C(7)—N(10)—C(8)	110.5 (10)
		P(4)—N(11)—C(9)	120.9 (11)
		P(4)—N(11)—C(10)	119.3 (11)
		C(9)—N(11)—C(10)	109.5 (11)
		N(9)—C(11)—C(12)	101.2 (15)
		N(3)—C(13)—C(14)	111.0 (11)

Table 3. *Exocyclic P—N lengths and sums of interbond angles*

	P—N bond length	Sum of interbond angles
N(6)	1.66 Å	358.6°
N(7)	1.72	345.2
N(8)	1.64	359.4
N(9)	1.69	350.4
N(10)	1.65	357.2
N(11)	1.66	349.6
N(3)	1.74 (mean)	336.8
P ₃ N ₃ (NMe ₂) ₆ ^a		
	1.654	350
	1.648	360
P ₄ N ₄ (NMe ₂) ₈ ^b		
	1.69	349.5
	1.67	358.5

(a) Rettig & Trotter (1973). (b) Bullen (1962).

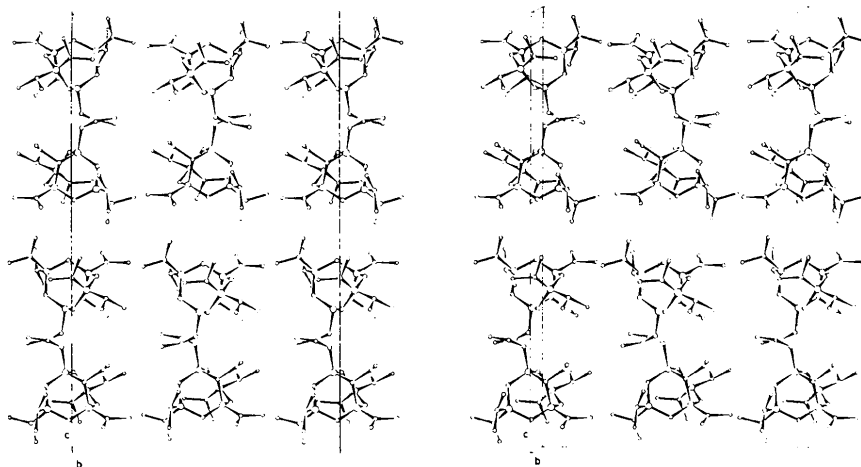


Fig. 2. Stereoscopic projection of the unit cell.

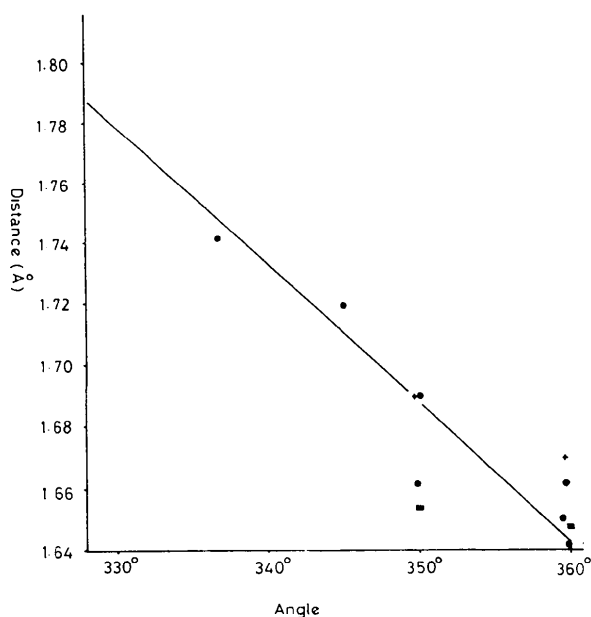


Fig. 3. Plot of the sum of the interbond angles at the exocyclic nitrogen atoms against the corresponding P-N bond length; (●) the title compound, (■) $P_3N_3(NMe_2)_6$ (Rettig & Trotter, 1973), (+) $P_4N_4(NMe_2)_8$ (Bullen, 1962).

an sp^2 N atom, the corresponding P-N length is about 1.79 Å, close to the 1.80 Å observed for a P-N single bond in a cyclic diphosphazene (Cameron, Howlett & Prout, 1977). From Fig. 3, the range of values for this exocyclic bond length is 1.64–1.79 Å. The difference in covalent radius between an sp^2 and sp^3 atom is about 0.03 Å (Coulson, 1961), and so the full extent of the range cannot be attributed to only this difference and other σ -bond effects (Craig & Paddock, 1971). It would appear therefore that there is some π interaction along the bond which is greatest when the N atom has an sp^2 configuration. Most probably, this is the $p\pi-d\pi$ interaction between the N orbital containing the lone pair electrons and an unoccupied d orbital on the P

atom. In the present structure the varying needs to relieve steric and crystal packing forces are probably responsible for the variation from pyramidal to trigonal planar configuration of the N atoms. There are no unusually short non-bonded contacts but from Fig. 2 it is clear that those N atoms that have an obvious pyramidal configuration are accommodating to the approach of adjacent atoms.

The C-N lengths of the dimethylamine and ethylamine groups are in the range 1.43–1.54 Å and 1.50–1.56 Å respectively; the e.s.d.'s of the C atom positions are large and little significance can be attached to these differences.

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