

The Structure of 9-Methyl-1,3,3,5,7,7-hexakis(methylamino)bicyclo[3.3.1]tetra(phosphazene)

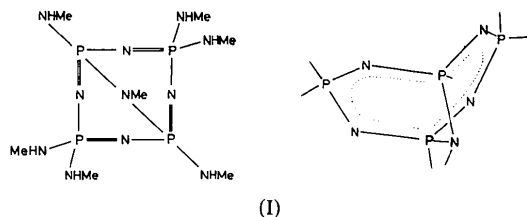
BY T. STANLEY CAMERON, RUTH E. CORDES AND FLORENCE A. JACKMAN

Department of Chemistry, Dalhousie University, Halifax, Nova Scotia B3H 4J3, Canada

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Abstract. $C_7H_{27}N_{11}P_4$, orthorhombic, $Pbcn$, $a = 10.49$ (1), $b = 18.44$ (2), $c = 18.93$ (2) Å, $Z = 8$, $D_c = 1.38$ Mg m⁻³, μ (Cu $K\alpha_1$) = 3.784 mm⁻¹, $\lambda = 1.54051$ Å. The structure was solved by an application of the tangent formula and refined by a least-squares method to $R = 0.07$. The molecule is a bicyclic phosphazene with a methylamine group bridging two P atoms. The two P–N bond lengths in the bridge are equivalent and significantly longer than any other P–N bonds in the compounds.

Introduction. In the structure of the bicyclic phosphazene $N_4P_4(NMe_2)_5(NHEt)(NEt)$, where the ethylamine group bridges two P atoms, the P–N bond lengths in the bridge are unusually long (1.73, 1.76 Å) and possibly non-equivalent (Cameron & Mannan, 1977). The present structure (I) has been determined in order to confirm the lengths of the P–N bridging bonds and to see whether they are significantly different when the two P atoms are equivalently substituted.



The crystals were provided by S. S. Krishnamurthy, Indian Institute of Science, Bangalore, India (Krishnamurthy, Ramachandran & Woods, 1979). The crystal system and approximate cell dimensions were determined from Weissenberg photographs. Systematic extinctions $0kl, k = 2n + 1; h0l, l = 2n + 1; hk0, h + k = 2n + 1$ uniquely indicated space group $Pbcn$. The crystals have an unusually large mosaic spread which gave a poor resolution when the cell dimensions were refined from the circle angles of 12 general reflections with the Bragg angle 2θ in the range 70–75° and 2645 unique reflections were measured on a Picker FACS-1 four-circle diffractometer. Of these, 2091 had $I > 3\sigma(I)$. The data were reduced to a standard scale by the routine procedure (Cameron & Cordes, 1979) and

Table 1. Atomic parameters ($\times 10^4$, except $\times 10^3$ for hydrogen)

	x	y	z
P(1)	644 (1)	3736 (1)	6309 (1)
P(2)	832 (2)	3788 (1)	4833 (1)
P(3)	478 (2)	2466 (1)	5519 (1)
P(4)	-1467 (1)	2848 (1)	6434 (1)
N(1)	786 (6)	4177 (3)	5593 (3)
N(2)	684 (5)	2917 (3)	4814 (4)
N(3)	1301 (5)	2890 (3)	6179 (3)
N(4)	-911 (5)	2350 (3)	5822 (3)
N(5)	-734 (5)	3585 (3)	6623 (3)
N(6)	1414 (5)	4165 (3)	6919 (3)
N(7)	-300 (6)	4171 (3)	4369 (3)
N(8)	2167 (6)	3951 (3)	4408 (3)
N(9)	1091 (6)	1670 (3)	5343 (4)
N(10)	-2928 (5)	3014 (4)	6183 (3)
N(11)	-1536 (7)	2421 (4)	7202 (3)
C(3)	2718 (6)	2888 (4)	6084 (4)
C(6)	2592 (7)	4569 (4)	6810 (5)
C(7)	-350 (8)	4012 (5)	3607 (5)
C(8)	2557 (8)	4693 (5)	4276 (5)
C(9)	973 (9)	1050 (5)	5804 (5)
C(10)	-3795 (8)	3418 (6)	6628 (5)
C(11)	-2153 (11)	1728 (6)	7274 (5)
H(31)	287 (7)	240 (2)	587 (3)
H(32)	305 (7)	327 (2)	575 (3)
H(33)	322 (6)	291 (3)	653 (2)
H(6)	99 (10)	411 (6)	738 (3)
H(61)	248 (6)	494 (3)	720 (2)
H(62)	266 (7)	485 (3)	636 (2)
H(63)	342 (5)	432 (4)	690 (3)
H(7)	-43 (13)	461 (7)	442 (7)
H(71)	-26 (9)	349 (2)	348 (6)
H(72)	-121 (3)	418 (5)	345 (5)
H(73)	30 (5)	429 (4)	333 (4)
H(8)	282 (5)	356 (3)	439 (3)
H(81)	301 (7)	485 (6)	472 (3)
H(82)	178 (5)	500 (5)	423 (4)
H(83)	313 (6)	480 (5)	386 (3)
H(9)	187 (4)	156 (4)	507 (3)
H(91)	180 (5)	78 (5)	583 (5)
H(92)	63 (8)	108 (6)	630 (2)
H(93)	37 (8)	73 (5)	552 (5)
H(10)	-326 (9)	261 (4)	589 (4)
H(101)	-338 (10)	383 (4)	688 (5)
H(102)	-456 (7)	361 (5)	637 (5)
H(103)	-407 (11)	305 (5)	698 (5)
H(11)	-107 (10)	257 (6)	764 (4)
H(111)	-164 (7)	141 (4)	695 (3)
H(112)	-222 (8)	149 (4)	775 (2)
H(113)	-303 (4)	177 (6)	707 (4)

were corrected for Lorentz and polarization but not for extinction or absorption factors.

The structure was solved by a multi-solution (Sheldrick, 1976) application of the tangent formula (Karle & Hauptman, 1958). The *E* map from the solution with the lowest Karle *R* factor clearly showed the positions of all the P, N and C atoms. The structure was refined by a large-block least-squares procedure, minimizing $\sum w(\Delta F)^2$, and converged at *R* = 0.07 for 2086 reflections (five reflections were removed on account of extinction effects) with weights calculated from $w = (\sigma^2 |F_o| + 0.0006 F_o^2)^{-1}$ where σ is the individual e.s.d. for each reflection calculated from the diffractometer counting statistics. Anisotropic temperature factors were used for all but the H atoms, and the positions of these were located from a difference Fourier synthesis calculated at an advanced stage in the refinement. The final atomic coordinates are given in Table 1.* The atomic scattering factors were those recorded in *International Tables for X-ray Crystallography* (1974), and were corrected for the real part of the anomalous-

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34117 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

P(1)—N(1)	1.587 (6)	P(4)—N(4)	1.589 (6)
P(1)—N(3)	1.723 (6)	P(4)—N(5)	1.602 (6)
P(1)—N(5)	1.587 (6)	P(4)—N(10)	1.633 (6)
P(1)—N(6)	1.615 (6)	P(4)—N(11)	1.654 (7)
P(2)—N(1)	1.607 (6)	N(3)—C(3)	1.498 (9)
P(2)—N(2)	1.615 (6)	N(6)—C(6)	1.457 (10)
P(2)—N(7)	1.637 (6)	N(7)—C(7)	1.471 (11)
P(2)—N(8)	1.643 (6)	N(8)—C(8)	1.451 (11)
P(3)—N(2)	1.587 (6)	N(9)—C(9)	1.445 (11)
P(3)—N(3)	1.709 (6)	N(10)—C(10)	1.446 (11)
P(3)—N(4)	1.581 (6)	N(11)—C(11)	1.439 (13)
P(3)—N(9)	1.636 (7)		
N(1)—P(1)—N(3)	107.7 (3)	N(4)—P(4)—N(10)	103.9 (3)
N(1)—P(1)—N(5)	119.6 (3)	N(4)—P(4)—N(11)	112.4 (3)
N(1)—P(1)—N(6)	108.2 (3)	N(5)—P(4)—N(10)	110.9 (3)
N(3)—P(1)—N(5)	105.0 (3)	N(5)—P(4)—N(11)	103.3 (3)
N(3)—P(1)—N(6)	110.2 (3)	N(10)—P(4)—N(11)	107.7 (3)
N(5)—P(1)—N(6)	105.9 (3)	P(1)—N(1)—P(2)	122.6 (4)
N(1)—P(2)—N(2)	117.4 (3)	P(2)—N(2)—P(3)	121.1 (4)
N(1)—P(2)—N(7)	105.5 (3)	P(1)—N(3)—P(3)	108.5 (3)
N(1)—P(2)—N(8)	112.5 (3)	P(1)—N(3)—C(3)	114.7 (4)
N(2)—P(2)—N(7)	110.3 (3)	P(3)—N(3)—C(3)	114.3 (4)
N(2)—P(2)—N(8)	104.6 (3)	P(3)—N(4)—P(4)	121.7 (4)
N(7)—P(2)—N(8)	106.0 (3)	P(1)—N(5)—P(4)	120.2 (4)
N(2)—P(3)—N(3)	107.8 (3)	P(1)—N(6)—C(6)	125.0 (5)
N(2)—P(3)—N(4)	120.1 (3)	P(2)—N(7)—C(7)	117.8 (5)
N(2)—P(3)—N(9)	104.2 (3)	P(2)—N(8)—C(8)	119.8 (5)
N(3)—P(3)—N(4)	105.2 (3)	P(3)—N(9)—C(9)	123.6 (6)
N(3)—P(3)—N(9)	111.2 (3)	P(4)—N(10)—C(10)	121.1 (6)
N(4)—P(3)—N(9)	108.4 (3)	P(4)—N(11)—C(11)	121.8 (6)
N(4)—P(4)—N(5)	118.4 (3)		

dispersion effect. The interatomic distances and bond angles are given in Table 2, and selected torsional angles in Table 3. Fig. 1 is a stereoscopic view of the molecule, and Fig. 2 shows the packing in the unit cell.

Discussion. The crystal is constructed from isolated molecules (Fig. 1) which have an eight-membered ring (PN)₄ with N(3) bridging between P(1) and P(3). The fragments of the ring on either side of the bridge are approximately planar (Table 3). The mean deviations from the least-squares best planes P(1)—N(1)—P(2)—N(2)—P(3) and P(3)—N(4)—P(4)—N(5)—P(1) are 0.014 (16) and 0.041 (53) Å. These two planes are inclined at 122.4 (8)°. The plane through atoms P(1)—N(3)—P(3) practically bisects this, making angles of 122.3 and 115.2° respectively with the previous two planes.

Table 3. Torsion angles (°) in the eight-membered ring

P(1)—N(1)—P(2)—N(2)	1.8 (5)
N(1)—P(2)—N(2)—P(3)	1.0 (5)
P(2)—N(2)—P(3)—N(4)	86.6 (5)
N(2)—P(3)—N(4)—P(4)	-97.5 (5)
P(3)—N(4)—P(4)—N(5)	13.9 (5)
N(4)—P(4)—N(5)—P(1)	-11.3 (5)
P(4)—N(5)—P(1)—N(1)	93.0 (5)
N(5)—P(1)—N(1)—P(2)	-91.3 (5)

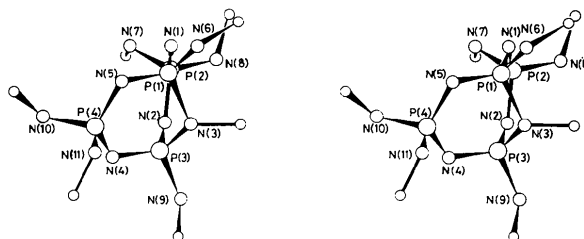


Fig. 1. A stereoscopic view of the unique molecule.

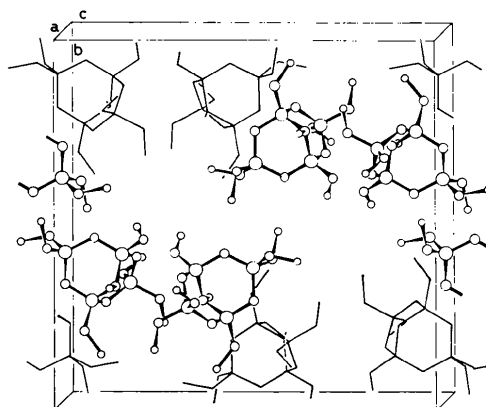


Fig. 2. The packing of the molecules in the unit cell.

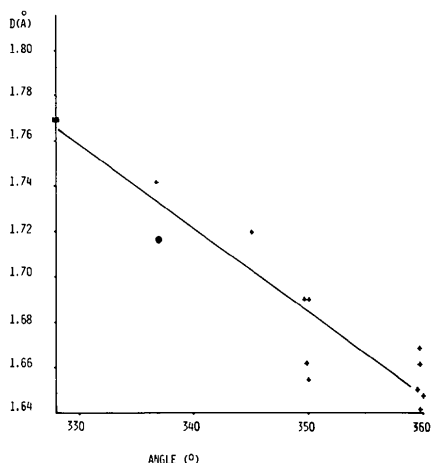


Fig. 3. A plot of the sum of the interbond angles at the exocyclic nitrogen atoms against the corresponding P—N bond length, (+) Cameron & Mannan (1977), (●) the title compound, (■) Cruickshank (1964).

Within the molecule there are three different types of P—N bond. Those within the eight-membered ring have lengths within the range 1.581 to 1.615, with mean 1.594 Å, and are not significantly different. The exocyclic lengths are in the range 1.615 to 1.654, with mean 1.637 Å, and with the exception of P(1)—N(6) (1.615 Å), these distances are also not significantly different. The P—N bond lengths in the bridge are long, as was observed before (Cameron & Mannan, 1977), and at 1.723 (6) and 1.709 (6) Å they are equivalent within the limits of the experimental data. The endocyclic P—N bond lengths are longer than those observed in the cyclotetra(phosphazene) chlorides, e.g. 1.553 (2) Å (Bullen & Dann, 1973), but are very similar to those observed in hexakis(dimethylamino)-cyclotri(phosphazene), mean 1.588 (2) Å (Rettig & Trotter, 1973). The exocyclic P—N bond lengths have been shown to vary according to the sum of the angles

at the N atom (Cameron & Mannan, 1977). In this case however, one of the three pendant atoms at N is a H atom which was difficult to locate accurately, so that no definite conclusions may be drawn. In $N_4P_4(NMe_2)_5(NHEt)(NEt)$ the mean P—N bond length in the bridge is 1.74 (1) Å and the sum of the bond angles at N is 336.8° , while in this compound the mean bond length is 1.716 (4) Å and the sum of the angles at N is 337.5° . With this extra value, the graph of P—N bond lengths against the sum of the angles at N (Cameron & Mannan, 1977) can be modified slightly so that it now passes closer to the point which corresponds to that normally accepted for a P—N single bond (Cruickshank, 1964) (Fig. 3).

The N—C bonds have reasonable lengths, the difference Fourier synthesis calculated at convergence shows no remarkable features, and there are no unusually short intermolecular distances.

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