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Decamethylcyclopentaphosphazene

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Abstract. $N_5P_5(CH_3)_{10}$; $F(000) = 400$; F.W. 375·24; triclinic, $P\bar{1}$; $a = 8{\cdot}959(2)$, $b = 10{\cdot}517(8)$, $c = 11{\cdot}296(9)$ Å, $\alpha = 93{\cdot}72(5)$, $\beta = 107{\cdot}29(5)$, $\gamma = 94{\cdot}86(3)°$; $Z = 2$; $D_c = 1{\cdot}237$ g cm^{-3}. Full-matrix least-squares refinement of 3307 reflexions collected with graphite-monochromatized Cu $K\alpha$ radiation on an Enraf–Nonius CAD-4 diffractometer by a moving-crystal moving-counter technique (range $3° \le \theta \le 70°$) led to $R = 0{\cdot}037$. The alternating P,N ten-membered ring has insignificantly different P–N bonds between 1·581 and 1·593 Å; NPN angles are 116·5 to 120·2° and PNP angles 131·8 to 135·7°.

Introduction. A crystal grown from the melt (Searle, Dyson, Ranganathan & Paddock, 1975) inside a sealed tube of diameter 0·2 mm was used for the data collection. Direct methods were used to solve the structure, which refined to $R = 0{\cdot}097$ with isotropic and $R = 0{\cdot}056$ with anisotropic temperature factors. The inclusion of the methyl H atoms at calculated positions, assuming a staggered arrangement with respect to the other C and the two ring N atoms, on the P atom of the C–P bond, reduced R to 0·037 for the observed reflexions ($R = 0{\cdot}059$ when 507 weak reflexions, not used in the least squares, were included). A difference synthesis confirmed the H coordinates.*

Discussion. The coordinates and thermal parameters for the non-hydrogen atoms are given in Table 1, the molecular dimensions in Tables 2 and 3.

The conformation of the alternating P,N ten-mem-

* The lists of structure factors and H coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32138 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Fractional coordinates* ($\times 10^4$) *of non-hydrogen atoms with anisotropic temperature factors* ($\times 10^4$) *and e.s.d.'s in parentheses*

The anisotropic temperature factors are of the form:
$\exp\{-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl)\}$.

	x	y	z	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{13}$	$2U_{23}$
P(1)	6081 (1)	4708 (1)	3256 (1)	386 (3)	374 (3)	364 (3)	85 (3)	143 (3)	67 (3)
P(2)	6883 (1)	2293 (1)	4269 (1)	395 (3)	365 (3)	429 (4)	49 (3)	167 (3)	82 (3)
P(3)	8649 (1)	1018 (1)	2847 (1)	398 (4)	305 (3)	376 (3)	65 (3)	77 (3)	11 (3)
P(4)	7435 (1)	2002 (1)	455 (1)	573 (4)	408 (4)	323 (3)	75 (3)	99 (3)	−2 (3)
P(5)	8122 (1)	4590 (1)	1661 (1)	450 (4)	359 (3)	429 (4)	24 (3)	201 (3)	25 (3)
N(1)	6617 (3)	3763 (2)	4315 (2)	578 (14)	424 (13)	412 (12)	135 (10)	175 (11)	94 (10)
N(2)	8398 (3)	1913 (2)	3942 (2)	394 (12)	499 (13)	478 (13)	39 (10)	127 (10)	−56 (10)
N(3)	7493 (3)	1022 (2)	1480 (2)	561 (14)	453 (13)	414 (12)	−13 (11)	35 (11)	49 (10)
N(4)	8365 (3)	3388 (2)	838 (2)	603 (15)	436 (13)	571 (14)	59 (11)	310 (12)	1 (11)
N(5)	6538 (3)	4516 (2)	2013 (2)	421 (12)	585 (14)	357 (11)	57 (10)	134 (10)	35 (10)
C(1)	6749 (4)	6292 (3)	4047 (3)	905 (24)	434 (16)	541 (18)	106 (16)	255 (17)	24 (14)
C(2)	3979 (4)	4684 (4)	2784 (3)	481 (18)	906 (25)	639 (20)	222 (17)	207 (15)	226 (18)
C(3)	5122 (4)	1322 (3)	3316 (4)	442 (18)	624 (21)	1111 (30)	−98 (15)	228 (19)	−66 (20)
C(4)	7088 (4)	1889 (3)	5833 (3)	917 (26)	740 (22)	664 (21)	315 (19)	451 (20)	380 (18)
C(5)	8512 (5)	−635 (3)	3175 (3)	959 (26)	371 (16)	683 (21)	116 (16)	70 (19)	111 (15)
C(6)	10681 (4)	1395 (3)	2941 (3)	452 (16)	697 (21)	660 (20)	127 (15)	187 (15)	−69 (16)
C(7)	8225 (6)	1285 (4)	−690 (3)	1439 (39)	699 (24)	610 (22)	195 (24)	518 (24)	−80 (18)
C(8)	5383 (4)	2043 (4)	−352 (3)	739 (24)	757 (24)	697 (23)	34 (19)	−139 (19)	193 (19)
C(9)	9811 (4)	4908 (4)	3029 (3)	415 (17)	787 (23)	821 (24)	−44 (16)	135 (16)	−195 (19)
C(10)	8204 (5)	5948 (3)	787 (4)	1322 (35)	467 (18)	924 (27)	142 (20)	701 (26)	197 (18)

bered ring (Fig. 1) is very similar to that of the $[N_5P_5(CH_3)_{10}H_2]^{2+}$ cation (Calhoun & Trotter, 1974); a view of the neutral molecule along P(4)—N(3) shows that the P and N atoms are eclipsed in pairs so that the ring has the appearance of a question mark. All P—N distances, which are not significantly different, lie between 1·581 and 1·593 Å and the NPN and PNP angles, none of which is re-entrant, have a spread of 4·1 and 4·5° respectively.

Table 2. *Interatomic distances* (Å) *and angles* (°), *with e.s.d.'s in parentheses*

P(1)—N(1)	1·581 (3)	P(1)—C(1)	1·806 (3)
P(1)—N(5)	1·593 (2)	P(1)—C(2)	1·796 (3)
P(2)—N(1)	1·584 (2)	P(2)—C(3)	1·806 (3)
P(2)—N(2)	1·585 (3)	P(2)—C(4)	1·804 (4)
P(3)—N(2)	1·586 (3)	P(3)—C(5)	1·804 (3)
P(3)—N(3)	1·583 (2)	P(3)—C(6)	1·800 (3)
P(4)—N(3)	1·592 (3)	P(4)—C(7)	1·802 (5)
P(4)—N(4)	1·582 (2)	P(4)—C(8)	1·799 (4)
P(5)—N(4)	1·588 (3)	P(5)—C(9)	1·801 (3)
P(5)—N(5)	1·581 (3)	P(5)—C(10)	1·796 (4)
Mean	1·586 (4)*	Mean	1·801 (4)*
N(1)—P(1)—N(5)	119·98 (13)	N(1)—P(1)—C(1)	104·68 (13)
N(2)—P(2)—N(1)	117·38 (14)	N(1)—P(1)—C(2)	109·64 (15)
N(2)—P(3)—N(3)	118·96 (13)	N(5)—P(1)—C(1)	112·44 (15)
N(3)—P(4)—N(4)	120·17 (13)	N(5)—P(1)—C(2)	105·93 (14)
N(4)—P(5)—N(5)	116·46 (14)	N(1)—P(2)—C(3)	110·79 (14)
Mean	118·7 (1·8)*	N(1)—P(2)—C(4)	104·09 (17)
		N(2)—P(2)—C(3)	111·78 (16)
C(1)—P(1)—C(2)	102·91 (17)	N(2)—P(2)—C(4)	106·97 (17)
C(3)—P(2)—C(4)	104·67 (19)	N(2)—P(3)—C(5)	110·20 (17)
C(5)—P(3)—C(6)	104·22 (18)	N(2)—P(3)—C(6)	105·09 (14)
C(7)—P(4)—C(8)	104·82 (20)	N(3)—P(3)—C(5)	104·64 (14)
C(9)—P(5)—C(10)	104·90 (18)	N(3)—P(3)—C(6)	112·85 (16)
Mean	104·3 (0·8)*	N(3)—P(4)—C(7)	107·67 (17)
		N(3)—P(4)—C(8)	105·65 (17)
P(1)—N(1)—P(2)	132·65 (16)	N(4)—P(4)—C(7)	104·88 (18)
P(2)—N(2)—P(3)	133·31 (14)	N(4)—P(4)—C(8)	112·57 (16)
P(3)—N(3)—P(4)	131·16 (16)	N(4)—P(5)—C(9)	108·51 (16)
P(4)—N(4)—P(5)	131·84 (20)	N(4)—P(5)—C(10)	106·33 (18)
P(5)—N(5)—P(1)	135·67 (14)	N(5)—P(5)—C(9)	111·37 (16)
Mean	132·9 (1·7)*	N(5)—P(5)—C(10)	108·53 (20)

* Root-mean-square deviation from the mean.

The non-planarity of the ring may be seen in Table 3(*c*) and is in contrast to the $N_5P_5Cl_{10}$ ring (Schlueter & Jacobson, 1968), which is planar owing to very large angles at the N atoms, two of which are re-entrant. Bond lengths and angles are compared with other ten-membered P—N rings and with other methylphosphazenes in Table 4. Agreement is good for the P—C lengths in all the methyl compounds (Calhoun & Trotter, 1974; Dougill, 1961) and for the average NPN and CPC angles for all the neutral phosphazenes. The variation in the PNP angle found in $N_5P_5Cl_{10}$ (Schlueter & Jacobson, 1968) and $N_5P_5Br_{10}$ (Hartsuiker & Wagner, 1972), allowing flexibility in the ring, is absent here; the values are internally consistent and agree with that found in $N_4P_4(CH_3)_8$ (Dougill, 1961).

Fig. 2 shows the unit cell and the short intermolecular distances; there appear to be no very short C · · · C distances, as found in $N_4P_4(CH_3)_8$.

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Table 3. *Dihedral angles, torsion angles and deviations from least-squares plane*

(*a*) Dihedral angles (°)

N(5)P(1)N(1)	C(1)P(1)C(2)	−85·96
N(2)P(2)N(1)	C(3)P(2)C(4)	−90·86
N(3)P(3)N(2)	C(5)P(3)C(6)	−94·62
N(4)P(4)N(3)	C(7)P(4)C(8)	+93·21
N(5)P(5)N(4)	C(9)P(5)C(10)	−90·11

(*b*) Torsion angles (°)

P(2)—N(5)—P(5)—N(4)	128·20	(108·1)*
N(5)—P(5)—N(4)—P(4)	−10·99	(20·7)
P(5)—N(4)—P(4)—N(3)	−67·97	(−90·9)
N(4)—P(4)—N(3)—P(3)	−16·41	(−11·1)
P(4)—N(3)—P(3)—N(2)	79·28	(60·0)
N(3)—P(3)—N(2)—P(2)	39·14	(128·7)
P(3)—N(2)—P(2)—N(1)	−119·19	(−150·4)
N(2)—P(2)—N(1)—P(1)	73·41	(33·9)
P(2)—N(1)—P(1)—N(5)	−32·11	(−62·3)
N(1)—P(1)—N(5)—P(5)	−64·04	(−20·0)

(*c*) Deviations from the least-squares plane through the P atoms. The equation is referred to the crystal axes and *x*,*y*,*z* are in Å.

P(1) 0·3205	P(2) 0·1158	P(3) −0·4675	P(4) 0·7457	P(5) −0·7146
N(1) −0·0843	N(2) −0·7910	N(3) 0·7012	N(4) −0·3734	N(5) 0·3524

$$(0{\cdot}7998)x + (0{\cdot}3141)y + (0{\cdot}5113)z - (6{\cdot}7048) = 0.$$

* Values for $[N_5P_5(CH_3)_{10}H_2]^{2+}$.

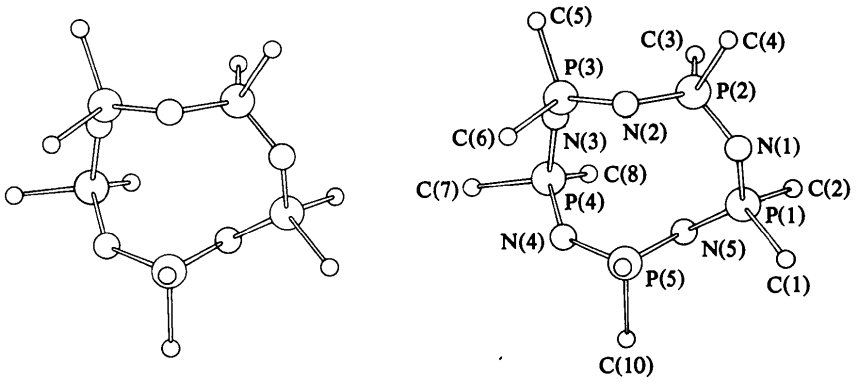

Fig. 1. The molecule of $N_5P_5(CH_3)_{10}$. [Numbering is the same as in Calhoun & Trotter (1974).]

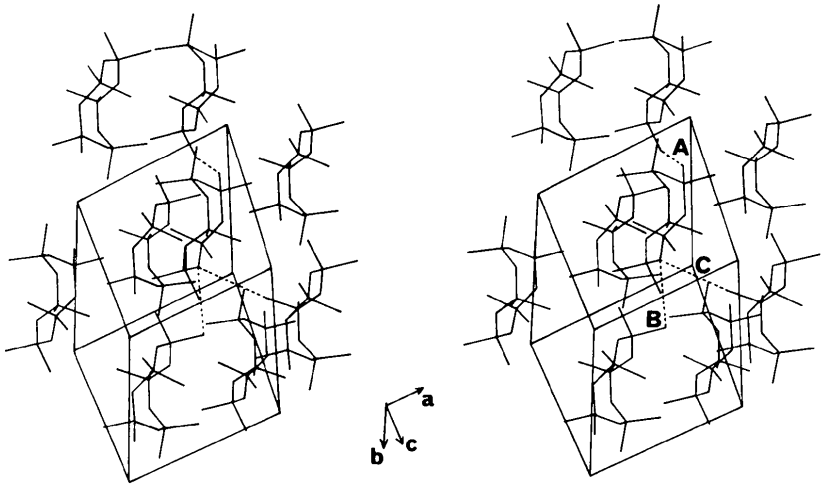

Fig. 2. Stereo pair of the unit cell. $A = 3{\cdot}79$ Å, $C(7)_{(000)}$–$C(2)_{(010)}$; $B = 3{\cdot}77$ Å, $N(5)_{(000)}$–$C(1)_{(111)}$; $C = 3{\cdot}77$ Å, $N(5)_{(000)}$–$C(4)_{(211)}$.

Table 4. *Range and average values of bond lengths* (Å) *and angles* (°) *in some phosphazenes*

	$N_4P_4(CH_3)_8$	$N_5P_5(CH_3)_{10}$	$N_5P_5(CH_3)_{10}H_2^{2+}$	$N_5P_5Cl_{10}$	$N_5P_5Br_{10}$
P–N					
Range	1·591–1·601	1·581–1·593	1·533–1·687	1·488–1·553	1·541–1·606
Mean	1·596	1·586	1·611	1·526	1·571
P–C					
Range	1·802–1·808	1·796–1·806	1·788–1·812		
Mean	1·805	1·801	1·802		
N–P–N					
Range		116·5–120·7	108·2–116·6	116·0–121·2	113·7–121·1
Mean	119·8	118·7	112·7	118·4	116·8
P–N–P					
Range		131·8–135·7	127·3–148·3	133·6–159·0	129·7–143·8
Mean	132·0	132·9	135·7	148·6	135·9
C–P–C					
Range		102·9–104·9	105·7–108·8		
Mean	104·1	104·3	107·4		

References

CALHOUN, H. P. & TROTTER, J. (1974). *J. Chem. Soc. Dalton*, pp. 382–386.

DOUGILL, M. W. (1961). *J. Chem. Soc.* pp. 5471–5479.

HARTSUIKER, J. G. & WAGNER, R. A. (1968). *J. Chem. Soc. Dalton*, pp. 1069–1073.

SCHLUETER, A. W. & JACOBSON, R. A. (1968). *J. Chem. Soc. (A)*, pp. 2317–2325.

SEARLE, H. T., DYSON, J., RANGANATHAN, T. N. & PADDOCK, N. L (1975). *J. Chem. Soc. Dalton*, pp. 203–208.