

2,2-Dimethyl-4,4,6,6-tetraphenylcyclotri(phosphazene)

BY M. W. DOUGILL

Department of Chemical Sciences, The Polytechnic, Huddersfield HD1 3DH, England

N. L. PADDOCK

Department of Chemistry, University of British Columbia, 2036 Main Mall, University Campus, Vancouver, BC, Canada V6T 1Y6

AND B. SHELDRIK

Astbury Department of Biophysics, University of Leeds, LS2 9JT, England

(Received 25 February 1980; accepted 16 June 1980)

Abstract. $C_{26}H_{26}N_3P_3$, $N_3P_3(CH_3)_2(C_6H_5)_4$, $F(000) = 992$, $M_r = 473.44$, monoclinic, $P2_1/n$, $a = 9.298$ (4), $b = 20.542$ (10), $c = 13.373$ (8) Å, $\beta = 102.14$ (5)°, $Z = 4$, $D_c = 1.259$, $D_m = 1.27$ Mg m⁻³, $\mu(Cu K\alpha) = 1.27$ mm⁻¹. Full-matrix least-squares refinement of 4463 reflexions collected with graphite-monochromatized Cu $K\alpha$ radiation on an Enraf–Nonius CAD-4 diffractometer by a moving-crystal moving-counter technique (range $3^\circ < \theta < 70^\circ$) led to $R = 0.081$. The P–N bond length is 1.601 Å, the NPN angles are 116.2° (PMe₂) and 118.4° (PPh₂) and the PNP angles are 120.0° (between PPh₂ groups) and 121.5°. The N_3P_3 ring is significantly non-planar.

Introduction. The crystal used was prepared by Dr R. T. Oakley (Gallicano, Oakley & Paddock, 1980), and measured $0.3 \times 0.3 \times 0.4$ mm. The coordinates of the P atoms were obtained from a three-dimensional Patterson synthesis, and the structure was solved from an electron density map using phases calculated from them, with the use of published scattering factors (*International Tables for X-ray Crystallography*, 1962). The structure was refined with isotropic temperature factors to $R = 0.152$, then with anisotropic factors to $R = 0.097$. The inclusion of H atoms at positions calculated after each cycle of refinement led to $R = 0.081$ for observed reflexions, or 0.083 if 167 weak reflexions which were not used in the refinement were included.* The coordinates of the H atoms coincided with maxima on a difference synthesis.

Discussion. The coordinates of the non-hydrogen atoms are given in Table 1, and the molecular

dimensions in Table 2. Figs. 1 and 2 show the molecular geometry and packing respectively. The angular positions of the four phenyl groups appear to be controlled sterically, the shortest intramolecular

Table 1. Fractional coordinates (for P $\times 10^5$, for N, C $\times 10^4$) and U_{eq} ($\times 10^4$) of the non-hydrogen atoms, with e.s.d.'s in parentheses

	x	y	z	U_{eq} (Å ²)*
P(1)	23869 (12)	5961 (5)	-915 (8)	302 (6)
P(2)	42175 (12)	15671 (4)	9256 (8)	289 (5)
P(3)	32060 (12)	6005 (5)	20485 (8)	303 (6)
N(1)	3595 (4)	1158 (2)	-91 (3)	395 (23)
N(2)	4107 (4)	1262 (2)	2004 (3)	376 (24)
N(3)	2251 (4)	323 (2)	1003 (3)	392 (23)
C(1)	616 (6)	890 (3)	-722 (5)	525 (35)
C(2)	2772 (6)	-70 (2)	-858 (4)	526 (35)
C(3)	3339 (5)	2361 (2)	848 (4)	410 (27)
C(4)	3465 (7)	2739 (3)	1697 (5)	617 (40)
C(5)	2762 (8)	3351 (3)	1650 (6)	812 (52)
C(6)	1936 (7)	3564 (3)	732 (5)	819 (47)
C(7)	1793 (7)	3191 (3)	-130 (5)	731 (38)
C(8)	2499 (6)	2580 (2)	-84 (4)	544 (31)
C(9)	6105 (5)	1771 (2)	953 (3)	335 (24)
C(10)	7113 (6)	1829 (3)	1843 (5)	607 (39)
C(11)	8556 (7)	2026 (4)	1863 (6)	776 (55)
C(12)	8982 (6)	2168 (3)	960 (6)	769 (54)
C(13)	8000 (7)	2105 (3)	73 (6)	835 (48)
C(14)	6546 (6)	1909 (3)	34 (4)	565 (32)
C(15)	1987 (5)	719 (2)	2918 (3)	407 (26)
C(16)	1974 (7)	1281 (2)	3484 (4)	625 (37)
C(17)	995 (8)	1356 (3)	4122 (5)	882 (47)
C(18)	3 (7)	873 (4)	4192 (5)	891 (54)
C(19)	24 (7)	301 (4)	3648 (5)	801 (57)
C(20)	997 (6)	221 (3)	3008 (4)	603 (36)
C(21)	4469 (5)	-20 (2)	2658 (3)	374 (24)
C(22)	4618 (7)	-607 (2)	2146 (4)	554 (40)
C(23)	5661 (8)	-1057 (3)	2595 (5)	719 (47)
C(24)	6532 (7)	-949 (3)	3547 (5)	692 (36)
C(25)	6389 (6)	-377 (3)	4062 (4)	520 (31)
C(26)	5351 (6)	84 (2)	3613 (3)	432 (28)

* Lists of structure factors, thermal parameters and H-atom coordinates, and additional details of the molecular geometry have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35424 (28 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

* $U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \bar{a}_i \bar{a}_j$, where \bar{a}_i is the direct cell constant, and $U_{ij} = \exp[-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl)]$.

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

P(1)—N(1)	1.610 (4)	P(1)—C(1)	1.790 (6)
P(1)—N(3)	1.599 (4)	P(1)—C(2)	1.791 (5)
P(2)—N(1)	1.601 (4)	P(2)—C(3)	1.818 (4)
P(2)—N(2)	1.596 (4)	P(2)—C(9)	1.797 (4)
P(3)—N(2)	1.604 (4)	P(3)—C(15)	1.804 (5)
P(3)—N(3)	1.597 (4)	P(3)—C(21)	1.808 (4)
Mean	1.601 (5)*	Mean (to Ph)	1.807 (9)*
N(1)—P(1)—N(3)	116.2 (2)	C(3)—P(2)—C(9)	102.6 (2)
N(1)—P(2)—N(2)	118.8 (2)	C(15)—P(3)—C(21)	103.9 (2)
N(2)—P(3)—N(3)	117.9 (2)	P(1)—N(1)—P(2)	120.3 (2)
C(1)—P(1)—C(2)	105.2 (3)	P(2)—N(2)—P(3)	120.0 (2)
		P(3)—N(3)—P(1)	122.8 (3)

* R.m.s. deviation from mean.

Table 3. *Mean geometry of phenyl groups*

Group numbering: (1) C(3–8); (2) C(9–14); (3) C(15–20); (4) C(21–26). Mean planes are weighted by standard deviations of the coordinates; figures in parentheses are r.m.s. deviations from the mean.

Group	C—C (Å)	δ (C—C—C) (°)*	Δ (Å)†
(1)	1.39 (2)	0.67	0.0007 (5)
(2)	1.38 (3)	1.57	0.0014 (14)
(3)	1.383 (9)	0.78	0.007 (4)
(4)	1.388 (11)	0.96	0.004 (3)

* R.m.s. deviations from 120.00°.

† R.m.s. absolute deviations from the mean plane.

non-bonded C—C distances being normal, typically C(12)···C(8) 3.90 Å. The absence of steric strain among the phenyl groups is confirmed by the near-equality of the P—C—C angles [120.5 (1.5)°]. There are no unusual features in the geometry of the phenyl groups (Table 3). There is a small difference in length between the P—(CH₃) and P—(C₆H₅) bonds, which can be ascribed to the difference in σ hybridization at P implied by the C—P—C angles. The mean length of the P=N bonds is intermediate between those in N₃P₃Ph₆ (1.597 Å) (Ahmed, Singh & Barnes, 1969) and in N₃P₃Me₆ (1.605 Å) (Oakley, Paddock, Rettig & Trotter, 1977). Because the electronegativities of the methyl and phenyl groups do not differ greatly, there is no firm indication of the systematic bond-length inequalities found in N₃P₃Ph₄Cl₂ (Mani, Ahmed & Barnes, 1966), in N₃P₃Ph₂Cl₄ (Mani, Ahmed & Barnes, 1965) and in N₃P₃Ph₃F₄ (Allen, Faught, Moeller & Paul, 1969). The distinction between the two types of substituent is apparent in the N—P—N angles. The electron density in the P—N bonds is more remote from the less electronegative PMe₂ group than it is from the PPh₂ group, and the angle at the PMe₂ group is consequently the smaller, by 2.2°. The sum of the internal angles in the N₃P₃ ring is 4.1° less than the 720° required for planarity. The description of the distortion is arbitrary, but four atoms [N(1), N(2), N(3), P(1)] are nearly coplanar (mean

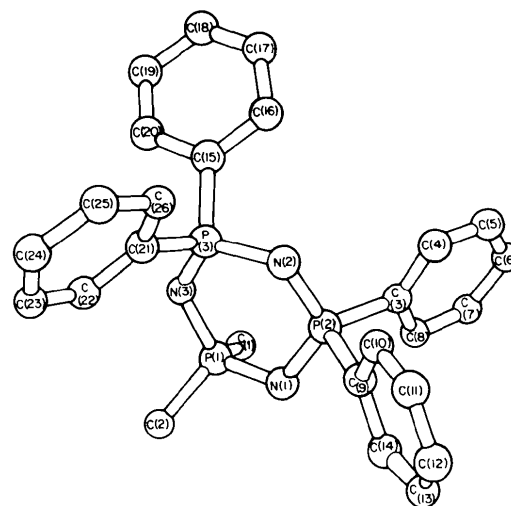
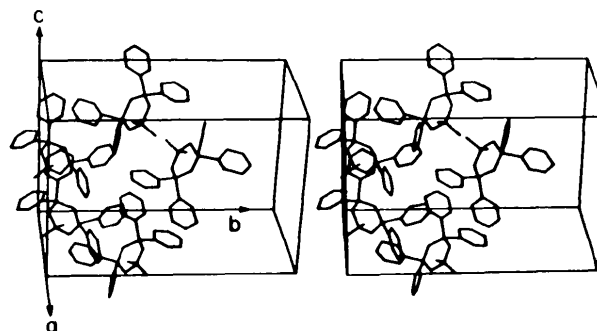
Fig. 1. The N₃P₃Me₂Ph₄ molecule.

Fig. 2. The molecular packing of N₃P₃Me₂Ph₄. The shortest intermolecular distances are C(2)($\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$)—C(22)($-\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$), 3.543 Å, and C(17)($\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$)—C(24)($-\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$), 3.565 Å.

deviation from weighted mean plane 0.05 Å). The other two P atoms are on opposite sides of the mean plane [P(2) 0.19; P(3) -0.21 Å].

We thank Dr R. T. Oakley for the crystals, Professor M. R. Truter for some of the computer programs, Mr D. Akrigg and the staff of the computing laboratories in Leeds University and Huddersfield Polytechnic for technical assistance, and the SRC and NSERC for support.

References

- AHMED, F. R., SINGH, P. & BARNES, W. H. (1969). *Acta Cryst.* **B25**, 316–328.
 ALLEN, C. W., FAUGHT, J. B., MOELLER, T. & PAUL, I. C. (1969). *Inorg. Chem.* **8**, 1719–1727.
 GALLICANO, K. D., OAKLEY, R. T. & PADDOCK, N. L. (1980). *J. Inorg. Nucl. Chem.* **42**, 932–924.
International Tables for X-ray Crystallography (1962). Vol. III, p. 202. Birmingham: Kynoch Press.
 MANI, N. V., AHMED, F. R. & BARNES, W. H. (1965). *Acta Cryst.* **19**, 693–698.
 MANI, N. V., AHMED, F. R. & BARNES, W. H. (1966). *Acta Cryst.* **21**, 375–382.
 OAKLEY, R. T., PADDOCK, N. L., RETTIG, S. J. & TROTTER, J. (1977). *Can. J. Chem.* **55**, 4206–4210.