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6-Oxo-2,2,4,4,6-pentaphenoxycyclotri-λ^5-phosphazane-1,3-diene

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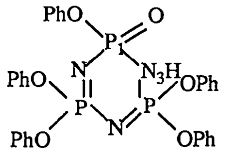
Abstract. $C_{30}H_{26}N_3O_6P_3$, $M_r = 617{\cdot}48$, monoclinic, $P2_1/n$, $a = 13{\cdot}200\,(4)$, $b = 16{\cdot}714\,(3)$, $c = 13{\cdot}438\,(9)$ Å, $\beta = 96{\cdot}38\,(3)°$, $V = 2946{\cdot}3$ Å^3, $Z = 4$, $D_x = 1{\cdot}392$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, μ = 0·23 mm^{-1}, $F(000) = 1280$, $T = 293\,(1)$ K, $R = 0{\cdot}037$ for 4089 observed data with $I > 3\sigma(I)$. The P_3N_3 ring has a boat conformation with a P atom and an N atom 0·396 (1) and 0·118 (2) Å, respectively, out of the plane of the remaining atoms of the ring. One of the P atoms involves a double bond P═O [1·470 (1) Å] and a P—N single bond [1·683 (1) Å]. The P—O single bonds and P—N ring bonds range between 1·564 (1) and 1·594 (1) Å [mean 1·576 (1) Å] and 1·546 (1) and 1·607 (1) Å [mean 1·574 (1) Å], respectively.

Experimental. The title compound (1) was synthesized by the hydrolysis of pentaphenoxymonochlorocyclotriphosphazene, $N_3P_3(OC_6H_5)Cl$, in dioxane. Well formed prismatic crystals of the title compound were grown from a solution in acetone by slow evaporation at room temperature. A crystal of approximate size 0·42 × 0·50 × 0·36 mm was cut from a large plate for data collection. Accurate cell constants and an orientation matrix were determined by a least-squares refinement of the setting angles of 25 reflections with θ in the range 10–15°. Intensity data in the range $2 < \theta < 25°$ (h 0→15, k 0→19, l −15→15) were collected on an Enraf–Nonius CAD-4 diffractometer using the $\omega/2\theta$ scan method, variable scan speed (1·25–2·35° min^{-1}) and monochromatized Mo $K\alpha$ radiation. The intensities of three standard reflections measured every 2 h of exposure time did not show any decay of the crystal. The data were corrected for Lorentz, polarization and absorption effects (North, Phillips & Matthews, 1968); the max. and min. relative transmission coefficients were 0·99 and 0·91, respectively. Of the 5160 unique ($R_{\rm int} = 0{\cdot}011$) reflections, 4089 with $I > 3\sigma(I)$ were labeled observed and used in all subsequent calculations.



(1)

The structure was solved by direct methods in *MULTAN*82 (Main *et al.*, 1982) and refined by full-matrix least-squares calculations using F's initially with isotropic and finally with anisotropic temperature factors for the non-H atoms. A difference map calculated at an intermediate stage revealed the positions of H atoms which were included and allowed to refine with an overall fixed

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Table 1. *Final fractional coordinates and equivalent isotropic thermal parameters* ($Å^2$) *with e.s.d.'s in parentheses*

$$B_{eq} = (1/3)\sum_i\sum_j B_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
P1	0·47785 (4)	0·10896 (3)	0·07889 (4)	3·16 (1)
P2	0·45149 (4)	0·14162 (3)	0·27633 (4)	3·18 (1)
P3	0·60646 (4)	0·03802 (3)	0·24894 (4)	3·37 (1)
O1	0·4000 (1)	0·07032 (9)	0·0081 (1)	4·00 (3)
O2	0·5448 (1)	0·16197 (9)	0·0123 (1)	3·98 (3)
O3	0·3619 (1)	0·08847 (9)	0·3085 (1)	4·09 (3)
O4	0·4388 (1)	0·21797 (9)	0·3417 (1)	3·86 (3)
O5	0·7236 (1)	0·0543 (1)	0·2534 (1)	4·54 (4)
O6	0·6066 (1)	−0·05174 (9)	0·2845 (1)	4·24 (3)
N1	0·4409 (1)	0·1638 (1)	0·1630 (1)	3·46 (4)
N2	0·5527 (1)	0·0954 (1)	0·3165 (1)	3·50 (4)
N3	0·5599 (1)	0·0407 (1)	0·1333 (1)	3·27 (3)
C11	0·6439 (2)	0·1871 (1)	0·0437 (2)	3·83 (5)
C12	0·6612 (2)	0·2543 (2)	0·1016 (2)	4·85 (6)
C13	0·7601 (2)	0·2807 (2)	0·1248 (2)	6·23 (7)
C14	0·8395 (2)	0·2400 (2)	0·0915 (2)	6·85 (7)
C15	0·8214 (2)	0·1723 (2)	0·0348 (2)	6·30 (7)
C16	0·7229 (2)	0·1452 (2)	0·0104 (2)	5·05 (6)
C21	0·2583 (2)	0·1067 (1)	0·2848 (2)	4·17 (5)
C22	0·2063 (2)	0·1334 (2)	0·3600 (2)	5·47 (6)
C23	0·1034 (2)	0·1468 (2)	0·3399 (2)	6·98 (8)
C24	0·0543 (2)	0·1346 (2)	0·2483 (3)	7·18 (8)
C25	0·1069 (2)	0·1105 (3)	0·1743 (3)	8·06 (9)
C26	0·2115 (2)	0·0957 (2)	0·1906 (2)	6·45 (7)
C31	0·4989 (2)	0·2874 (1)	0·3388 (2)	3·70 (4)
C32	0·4585 (3)	0·3502 (2)	0·2868 (2)	6·51 (8)
C33	0·5131 (4)	0·4199 (2)	0·2869 (3)	9·7 (1)
C34	0·6057 (3)	0·4255 (2)	0·3380 (3)	9·19 (9)
C35	0·6469 (3)	0·3616 (2)	0·3917 (3)	8·17 (9)
C36	0·5915 (2)	0·2905 (2)	0·3923 (2)	5·76 (6)
C41	0·7809 (2)	0·0797 (2)	0·3422 (2)	3·75 (4)
C42	0·7992 (2)	0·1592 (2)	0·3536 (2)	5·16 (6)
C43	0·8569 (2)	0·1854 (2)	0·4390 (2)	6·73 (7)
C44	0·8940 (2)	0·1333 (3)	0·5088 (2)	7·64 (8)
C45	0·8763 (2)	0·0549 (3)	0·4962 (2)	7·89 (9)
C46	0·8182 (2)	0·0264 (2)	0·4123 (2)	6·01 (7)
C51	0·4856 (2)	0·0859 (1)	0·6928 (2)	3·89 (5)
C52	0·5472 (2)	0·1247 (2)	0·7661 (2)	5·05 (6)
C53	0·6350 (3)	0·1598 (2)	0·7416 (2)	6·28 (7)
C54	0·6616 (2)	0·1548 (2)	0·6464 (2)	6·37 (7)
C55	0·5986 (2)	0·1157 (2)	0·5751 (2)	5·85 (7)
C56	0·5101 (2)	0·0814 (2)	0·5965 (2)	4·82 (5)

Table 2. *Selected molecular dimensions and their e.s.d.'s*

P1	O1		1·470 (1)	P3	O6		1·574 (1)
P1	O2		1·594 (1)	P3	N2		1·546 (1)
P1	N1		1·574 (1)	P3	N3		1·607 (1)
P1	N3		1·683 (1)	O2	C11		1·394 (2)
P2	O3		1·577 (1)	O3	C21		1·402 (2)
P2	O4		1·569 (1)	O4	C31		1·408 (2)
P2	N1		1·558 (1)	O5	C41		1·405 (2)
P2	N2		1·585 (1)	O6	C51		1·408 (2)
P3	O5		1·564 (1)				
O1	P1	O2	105·81 (6)	O5	P3	N2	112·68 (7)
O1	P1	N1	118·07 (6)	O5	P3	N3	107·60 (6)
O1	P1	N3	110·69 (6)	O6	P3	N2	113·43 (7)
O2	P1	N1	108·33 (3)	O6	P3	N3	107·92 (6)
O2	P1	N3	104·49 (6)	N2	P3	N3	113·54 (6)
N1	P1	N3	108·56 (6)	P1	O2	C11	123·94 (9)
O3	P2	O4	100·09 (6)	P2	O3	C21	123·8 (1)
O3	P2	N1	114·38 (6)	P2	O4	C31	124·01 (9)
O3	P2	N2	105·12 (6)	P3	O5	C41	121·46 (9)
O4	P2	N1	110·52 (6)	P3	O6	C51	118·68 (9)
O4	P2	N2	110·12 (6)	P1	N1	P2	124·22 (8)
N1	P2	N2	115·43 (7)	P2	N2	P3	121·78 (7)
O5	P3	O6	100·74 (7)	P1	N3	P3	126·69 (7)

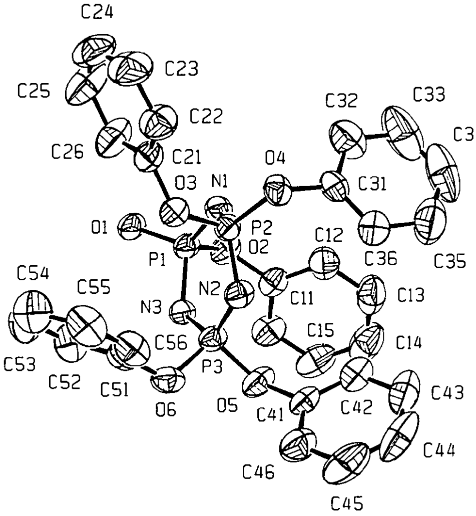

Fig. 1. The molecular structure of the title compound with the crystallographic numbering scheme.

temperature factor $B_{iso} = 5·0$ $Å^2$. The refinement converged with $R = 0·037$ and $wR = 0·055$, where $w = \{[\sigma^2(F_o)] + 0·040F_o)^2\}^{-1}$; the maximum shift/e.s.d. in the last cycle of refinement was $<0·1$ and $S = 2·218$. A final difference map showed no significant features with $\Delta\rho$ in the range $-0·26$ to $0·23$ e $Å^{-3}$. Scattering factors used in the calculations were taken from Cromer & Mann (1968) and Stewart, Davidson & Simpson (1965) and allowance was made for anomalous dispersion (Cromer & Liberman, 1970). Computer programs used in this study were from the *Structure Determination Package* (Frenz, 1985) and *ORTEP*II (Johnson, 1976).

Final fractional coordinates and equivalent isotropic thermal parameters with e.s.d.'s are given in Table 1.* Table 2 contains bond lengths and bond angles. Fig. 1 shows the molecular structure of the title compound with the crystallographic numbering scheme.

The tautomeric structure of this compound with an H atom attached to skeletal N atom rather than to a side group O atom is believed to represent the situation in a range of cyclic trimeric and polymeric phosphazenes in which an —OH group would be expected at phosphorus.

Related literature. Structures of 2,4,6-trimethoxy-1,3,5-trimethyl-2,4,6-trioxocyclotriphosphazane (Ansell & Bullen, 1968) and ammonium trimetaphosphimate methanol solvate (Attig & Mootz, 1976) have been reported.

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* Lists of structure factors, anisotropic thermal parameters, molecular dimensions including H atoms, least-squares-planes data and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53384 (52 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of (±)-(1*R**,6*S**)-1-Benzyloxy-8,11,11-trimethyl-6-phenylthiobicyclo[5.3.1]undec-7-en-3-one

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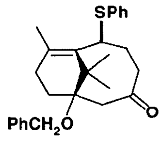
Abstract. $C_{27}H_{32}O_2S$, $M_r = 420\cdot61$, monoclinic, $P2_1/c$, $a = 8\cdot4756\,(13)$, $b = 14\cdot710\,(2)$, $c = 18\cdot425\,(3)$ Å, $\beta = 99\cdot575\,(13)°$, $V = 2265\cdot2\,(6)$ Å^3, $Z = 4$, $D_x = 1\cdot23$ g cm^{-3}, $\mu = 1\cdot5567$ cm^{-1}, Mo $K\alpha$, $\lambda = 0\cdot7107$ Å, $F(000) = 904$, $T = 298$ K, $R = 0\cdot0630$ for 2942 reflections $[F_o \geq 6\sigma(F_o)]$. The cyclooctane portion of the [5.3.1] ring system assumes the boat–chair conformation while the cyclohexene portion has the boat conformation. As has been observed in other [5.3.1]undecene systems, ring strain appears to cause a distortion of the geometry of the bridgehead alkene. The bond length C7—C8 [1·343 (5) Å] is long for an isolated C—C double bond. The C_{sp^2}—C_{sp^3} bond lengths at C7 are asymmetric with C7—C6 being 1·498 (5) Å while C7—C11 is 1·535 (5) Å. The maximum deviation from ideality for the torsion angles around the double bond is 16·2 (4)° (absolute value). This twist in the alkene group is reflected in the non-planarity of the group [max. deviation 0·193 (6) Å for C9] and in the dihedral angle between the nearly planar portions (C6, C7, C8, C11 and C7, C8, C9, C15), which is 9·4 (2)°.

Experimental. The bicyclo[5.3.1]undecene (1), which possesses the key structural subunit that is present in the taxane diterpenes (Martin, White & Wagner, 1982), was obtained by an anionic oxy-Cope rearrangement of a suitably substituted bicyclo-[2.2.2]octane (Martin, White, Wagner, Guinn, Tanaka, Assercq, Gluchowski, Austin & Dantanarayana, 1990). The data crystal was a colorless block that was cut from a larger crystal and had approximate dimensions 0·37 × 0·42 × 0·47 mm. Crystals were obtained by slow evaporation from ether. The data were collected at room temperature using graphite-monochromatized Mo $K\alpha$ radiation on a Picker diffractometer that was automated by the Krisel Control Corporation. Lattice parameters were obtained from least-squares refinement of 20 reflections with $27\cdot6 < 2\theta < 32\cdot3°$. Data were collected using the ω-scan technique (13 322 reflections, 6601 unique, $R_{\rm int} = 0\cdot0325$), with a 2θ range 4·0–60°, over a 1°ω scan at 6° min^{-1} ($h = -11\rightarrow11$, $k = -20\rightarrow20$, $l = 0\rightarrow25$). Three reflections (004, 060, 200) were remeasured every two hours to monitor instrument and crystal stability (maximum correction on I was < 1%; Henslee & Davis, 1975). The data were also corrected for Lp effects and secondary extinction but not for absorption. The secondary-extinction correction is of the form $F_{\rm corr} = F_c\{1 - [2\cdot64\,(2) \times 10^{-7}(F_c)^2/\sin\theta]\}$. The data reduction is



(1)