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The Structure of 1-*tert*-Butyl-2,2,3,4,4-pentamethylphosphetane 1-Oxide, C₁₂H₂₅OP

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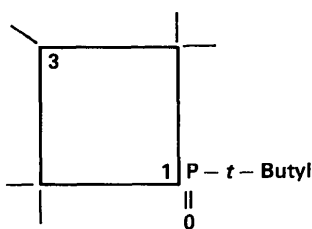
Abstract. $M_r = 216.30$, monoclinic, $P2_1/m$, $a = 6.137$ (2), $b = 12.181$ (4), $c = 9.005$ (3) Å, $\beta = 96.24$ (3)°, $V = 669.2$ (9) Å³, $Z = 2$, $D_m = 1.06$, $D_x = 1.07$ g cm⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 1.73$ cm⁻¹, $F(000) = 240$, $T = 295$ K, $R = 0.052$, $R_w = 0.051$, 1138 observed reflections. The single methyl group on C(3) is *trans* to the *tert*-butyl group on P. The four-membered ring is puckered with an angle of

19.2 (4)°, and the direction of ring puckering is such that the diaxial cross-ring interactions (CH₃ and O) between the substituents on P and C(3) are minimized.

Introduction. The structural analysis of 1-*tert*-butyl-2,2,3,4,4-pentamethylphosphetane 1-oxide (TPPO) was undertaken to confirm the stereochemistry, the direction and amount of puckering in the four-membered ring, and to compare the results with predictions based on previous results of similar compounds. The title compound was prepared by previously published methods (Gray & Cremer, 1972).

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Experimental. D_m by flotation in ethanol and methyl iodide mixture, colorless crystals of TPPO suitable for X-ray analysis obtained by recrystallization from cyclohexane. Crystal size $0.4 \times 0.1 \times 0.2$ mm. Nicolet $R3m$ diffractometer, graphite monochromator (Campagna, 1981), accurate unit-cell parameters from least-squares refinement of 25 reflections (θ range 10 – 15°), two standard reflections (040 and 200) measured every 120 min, 4% variation. Range of hkl : $0 \leq h \leq 8$, $0 \leq k \leq 16$, $-12 \leq l \leq 12$. 1845 data measured ($3 \leq 2\theta \leq 55^\circ$), 1138 with $I \geq 3\sigma(I)$; corrections for Lorentz and polarization effects (absorption and time decay ignored). Trial structure by direct methods and refined by full-matrix least-squares procedures, function minimized $\sum w(|F_o| - |F_c|)^2$ where $w = 1/[\sigma^2(F) + G(F)^2]$ and $G = 0.001$; non-hydrogen atoms anisotropic, H atoms located in ΔF map and idealized coordinates calculated and not refined, isotropic thermal parameters for H assigned as $1.2 \times$ value for C to which they are attached, $R = 0.052$ and $R_w = 0.051$, scattering factors for P, O, C and H from *International Tables for X-ray Crystallography* (1962), $S = 1.27$. In final cycle $(\Delta/\sigma)_{\max} = 0.006$; final difference map showed no peaks or depressions larger than $0.2 \text{ e } \text{\AA}^{-3}$. Calculations carried out with *SHELXTL* package on Nicolet $R3m$ crystallographic system (Sheldrick, 1980).*

Discussion. The atomic fractional coordinates with their standard deviations and U_{eq} values (Hamilton, 1959) are given in Table 1. The structure and numbering scheme of the title compound are shown in Fig. 1. Table 2 is a listing of selected interatomic distances and angles with their standard deviations.

The single methyl group on C(3) is *trans* to the *tert*-butyl group on phosphorus. The mirror plane passes through the P and O atoms as well as C atoms 1, 2, 3 and 8.

All phosphatane ring structures studied to date exhibit puckering of the four-membered ring. The amount of puckering in the four-membered ring is the angle between the planes defined by C(4)–P–C(4ⁱ) and

C(4)–C(3)–C(4ⁱ). The amount of puckering in TPPO is 19.2° . Qualitatively, the amount of puckering has been related to the number of substituent interactions (Fitzgerald, Campbell, Smith, Caughlan & Cremer, 1978). An interaction is considered to exist between substituents that are attached to adjacent ring atoms

Table 1. Final atomic coordinates for non-hydrogen atoms with *e.s.d.*'s in parentheses and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^2$)

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^*
P	0.14872 (16)	0.25000	1.15899 (11)	4.40 (3)
C(1)	0.2071 (6)	0.2500	0.9623 (4)	4.95 (12)
O(1)	–0.0920 (4)	0.2500	1.1621 (3)	7.28 (12)
C(2)	0.4480 (8)	0.2500	0.9371 (6)	6.82 (19)
C(3)	0.4541 (6)	0.2500	1.3442 (4)	4.92 (12)
C(4)	0.3087 (4)	0.1518 (2)	1.2834 (3)	5.26 (9)
C(5)	0.4391 (6)	0.0581 (3)	1.2235 (4)	7.79 (13)
C(6)	0.0942 (6)	0.1487 (3)	0.8908 (4)	8.11 (14)
C(7)	0.1589 (6)	0.1051 (4)	1.3931 (4)	8.85 (15)
C(8)	0.5367 (11)	0.2500	1.5090 (6)	8.37 (24)

* U_{eq} is defined as one third of the orthogonalized U_{ij} tensor.

Table 2. Selected bond angles ($^\circ$) and bond distances (\AA) with *e.s.d.*'s in parentheses

P–C(1)	1.845 (4)	C(4)–P–C(4 ⁱ)	80.7 (2)
P–O(1)	1.480 (3)	C(4)–C(3)–C(4 ⁱ)	100.5 (3)
P–C(4)	1.846 (3)	C(3)–C(4)–P	87.8 (2)
		C(1)–P–O(1)	108.5 (2)
C(1)–C(2)	1.520 (6)	C(1)–P–C(4)	115.9 (1)
C(1)–C(6)	1.523 (4)	C(4)–P–O(1)	117.0 (1)
		C(2)–C(1)–C(6)	110.0 (2)
C(3)–C(4)	1.556 (4)		
		C(2)–C(1)–P	115.9 (3)
C(3)–C(8)	1.518 (7)	C(6)–C(1)–P	106.2 (3)
C(4)–C(5)	1.531 (5)	P–C(4)–C(5)	108.4 (2)
C(4)–C(7)	1.526 (5)	P–C(4)–C(7)	122.3 (2)
		C(3)–C(4)–C(5)	114.8 (2)
		C(3)–C(4)–C(7)	113.4 (2)
		C(4)–C(3)–C(8)	117.6 (2)
		C(6)–C(1)–C(6)	108.2 (3)
		C(8)–C(4)–C(7)	109.0 (3)

Symmetry code: (i) $x, \frac{1}{2} - y, z$.

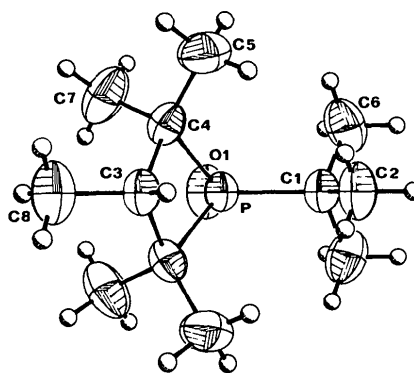
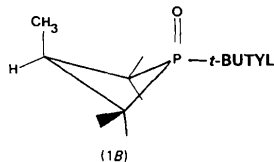
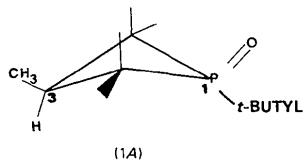


Fig. 1. The structure and numbering scheme for TPPO. Non-hydrogen atoms are represented as thermal ellipsoids scaled to enclose 50% probability. The hydrogen atoms are represented as spheres with 0.15 \AA radius in this illustration.

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39629 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

and *cis* to one another with respect to the phosphetane ring system. The C(5)–C(8) distance in TPPO is 3.010 (6) Å, which is substantially less than a 3.4 Å distance based on van der Waals radii (Bondi, 1964). The C(5)–O(1) distance is 3.019 (5) Å, which is also less than the sum of van der Waals radii (Bondi, 1964). Fitzgerald *et al.* (1978) found the amount of puckering to be in the range 19.6–24° for similar compounds with two methyl–methyl interactions. The amount of puckering in TPPO is very close to this range and may, in fact, represent a lower limit for compounds with two *cis* methyl–methyl interactions.

With respect to puckering direction or conformation preferences for TPPO, the following conformers may be considered.



TPPO exists in form (1A), and the C(8)–O distance of 4.69 (6) Å agrees well with similar compounds in which there is a single methyl group *trans* to a substituent on P (Fitzgerald *et al.*, 1978) and with distances measured from the molecular model of (1A).

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