

## References

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## Structure of 2,2,3,4,4-Pentamethyl-1-(1-naphthyl)- $\lambda^5$ -phosphetane 1-Oxide, C<sub>18</sub>H<sub>23</sub>OP

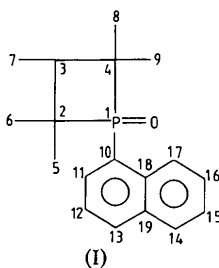
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**Abstract.**  $M_r = 286.36$ , orthorhombic,  $P2_12_12_1$ ,  $a = 8.009$  (2),  $b = 12.195$  (8),  $c = 16.425$  (9) Å,  $V = 1604.22$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.19$  g cm<sup>-3</sup>,  $\lambda(\text{Cu K}\alpha) = 1.54178$  Å,  $\mu = 14.38$  cm<sup>-1</sup>,  $F(000) = 616.00$ ,  $T = 298$  K,  $R = 0.0345$  for 1575 observed reflections. The four-membered ring is non-planar, with a puckering angle of 30.3°. The naphthyl ring, which is *cis* to the methyl substituent at C(3) in the four-membered ring, occupies a pseudo-equatorial position, to minimize cross-ring interaction with the methyl group.

**Introduction.** Structurally, phosphetanes are of twofold interest: firstly, comparison of phosphetane ring parameters with those of the carbocyclic analogues (cyclobutanes) provides valuable insight into the nature of ring strain in these compounds; and secondly, an empirical force field for phosphorus-containing compounds will need to be parameterized in such a way as to successfully describe these rather heavily strained heterocycles. The present investigation is concerned with a structural study of the highly substituted phosphetane (I).



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**Experimental.** Crystal  $ca$  0.40 × 0.43 × 1.25 mm, Enraf–Nonius CAD-4 diffractometer, take-off angle 5°, graphite-crystal-monochromatized Cu K $\alpha$  radiation, 25 reflections ( $28 < \theta < 33^\circ$ ) used to obtain cell dimensions by least-squares refinement, intensities of 1650 reflections ( $0 \leq h \leq 9$ ,  $0 \leq k \leq 14$ ,  $0 \leq l \leq 19$ ) measured,  $\omega$ - $2\theta$  scan,  $\theta_{\max} = 65^\circ$ ; three standard reflections monitored at intervals of 9000 s showed no variations in intensities; 1592 unique and 1575 observed reflections using  $I \geq 3\sigma(I)$  criterion. Lorentz and polarization corrections applied; direct methods, *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) revealed positions of all non-H atoms.  $R_{\text{int}} = 0.0074$  from merging equivalent reflections.  $F^2$  magnitudes used in  $E$  map and full-matrix least-squares refinement of non-H atoms with anisotropic temperature factors, and H atoms (taken from a difference map) isotropically. All H-atom positions, except that for C(3)H which was refined freely, constrained to a bonding distance of 0.981 (8) Å from their relevant C atoms; final  $R = 0.0345$ ,  $wR = 0.0356$ . Refinement of the structure of opposite chirality led to a final conventional  $R$  value of 0.0430; Hamilton's (1965) significance test confirms that our original (arbitrary) choice of enantiomer was correct. No absorption correction was applied but an empirical secondary extinction parameter refined to a final value of  $2.034 \times 10^{-2}$ . Weighting scheme for function  $w = 0.9839/(\sigma^2|F_o| + 0.002724F_o^2)$  used to minimize  $\sum w\Delta F^2$ ,  $S = 1.04$ . Max. peak height in final difference Fourier map = 0.239 e Å<sup>-3</sup>, ratio of max. LS shift to error 0.071. Form factors for non-H atoms from Cromer & Mann (1968), for H atoms from Stewart, Davidson & Simpson (1965). Calculations on an IBM 3033 computer at the University of Petroleum & Minerals using *SHELX76* (Sheldrick, 1976) programs.

**Discussion.** Fig. 1 is an ORTEPII diagram (Johnson, 1976) of the molecule illustrating 30% probability ellipsoids and the numbering scheme for the non-H atoms. For clarity, H atoms are omitted from the diagram, with the exception of C(3)H, which is depicted as a sphere of arbitrary radius 0.1 Å. The crystal packing is shown in Fig. 2. The positional parameters together with equivalent  $U$  values for non-H atoms are given in Table 1. Table 2 contains the bond lengths and valence angles involving non-H atoms.\*

The phosphetane ring in (I) is non-planar, with a puckering angle [defined as the supplement of the angle between planes C(2)–P(1)–C(4) and C(2)–C(3)–C(4)] of 30.3°. The naphthyl group, which is *cis* to the methyl substituent at C(3), is disposed pseudo-equatorially to the four-membered ring. This is consistent with the findings of Fitzgerald, Campbell, Smith, Caughlan & Cremer (1978) who rationalized the direction of ring puckering in symmetrically substituted

[at C(2) and C(4)] phosphetanes by considering the relative magnitudes of cross-ring interactions between substituents at C(3) and P in the two puckered forms. Thus, in the present instance, a pseudo-axially directed naphthyl group would have resulted in a large cross-ring interaction with the methyl group at C(3).

Table 1. Fractional coordinates ( $\times 10^4$ ) and equivalent isotropic thermal parameters ( $\text{\AA}^2 \times 10^3$ ) with *e.s.d.*'s in parentheses for non-H atoms

$$U_{eq} = \frac{1}{3}(\text{trace of orthogonalized } U_{ij} \text{ matrix}).$$

	$x$	$y$	$z$	$U_{eq}$
P(1)	9067 (1)	4681 (1)	7079 (1)	30
C(2)	7192 (3)	5318 (2)	6640 (1)	38
C(3)	6216 (3)	4791 (2)	7374 (1)	42
C(4)	7460 (3)	3836 (2)	7590 (1)	40
C(5)	6691 (4)	4892 (3)	5801 (2)	57
C(6)	7147 (4)	6570 (2)	6655 (2)	56
C(7)	4393 (3)	4495 (3)	7234 (2)	65
C(8)	7720 (5)	3716 (3)	8504 (2)	67
C(9)	6992 (4)	2729 (2)	7209 (2)	60
C(10)	10395 (2)	3970 (2)	6356 (1)	32
C(11)	10737 (3)	2868 (2)	6458 (1)	39
C(12)	11823 (3)	2318 (2)	5922 (2)	48
C(13)	12515 (3)	2846 (2)	5278 (2)	46
C(14)	12914 (3)	4546 (2)	4480 (1)	50
C(15)	12658 (4)	5649 (2)	4383 (2)	57
C(16)	11708 (4)	6222 (2)	4951 (2)	59
C(17)	10973 (4)	5699 (2)	5592 (1)	47
C(18)	11164 (3)	4553 (2)	5704 (1)	36
C(19)	12200 (3)	3976 (2)	5143 (1)	41
O(20)	10041 (2)	5406 (1)	7631 (1)	44

\* Lists of coordinates, bond lengths, and angles involving H atoms, together with structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42087 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

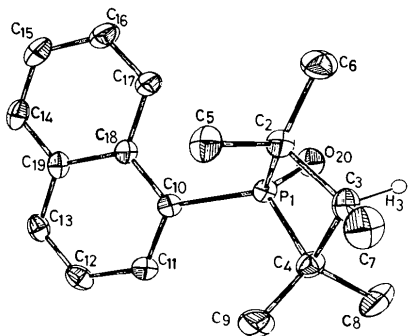


Fig. 1. ORTEP diagram of the  $C_{18}H_{23}PO$  molecule.

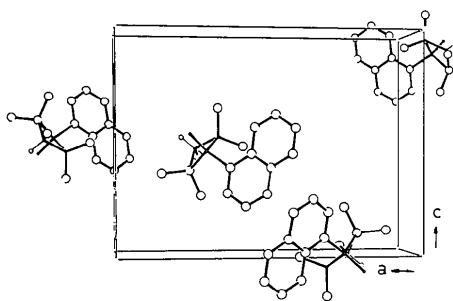


Fig. 2. The unit cell for  $C_{18}H_{23}PO$ .

Table 2. Bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) for non-H atoms, with *e.s.d.*'s in parentheses

P(1)–O(20)	1.487 (2)	C(10)–C(18)	1.425 (3)
P(1)–C(2)	1.838 (2)	C(11)–C(12)	1.408 (3)
P(1)–C(4)	1.849 (2)	C(12)–C(13)	1.356 (4)
P(1)–C(10)	1.815 (2)	C(13)–C(19)	1.418 (4)
C(2)–C(3)	1.574 (3)	C(14)–C(15)	1.370 (4)
C(2)–C(5)	1.526 (3)	C(14)–C(19)	1.413 (3)
C(2)–C(6)	1.527 (3)	C(15)–C(16)	1.393 (4)
C(3)–C(4)	1.573 (3)	C(16)–C(17)	1.365 (3)
C(3)–C(7)	1.521 (3)	C(17)–C(18)	1.419 (3)
C(4)–C(8)	1.522 (3)	C(18)–C(19)	1.425 (3)
C(4)–C(9)	1.534 (3)	C(3)H–C(3)	0.951 (27)
C(10)–C(11)	1.382 (3)		
C(2)–P(1)–O(20)	114.6 (1)	C(9)–C(4)–C(3)	113.8 (2)
C(4)–P(1)–O(20)	114.9 (1)	C(9)–C(4)–C(8)	110.5 (3)
C(4)–P(1)–C(2)	81.1 (1)	C(11)–C(10)–P(1)	120.1 (2)
C(10)–P(1)–O(20)	112.0 (1)	C(18)–C(10)–P(1)	120.5 (1)
C(10)–P(1)–C(2)	115.1 (1)	C(18)–C(10)–C(11)	119.4 (2)
C(10)–P(1)–C(4)	116.0 (1)	C(12)–C(11)–C(10)	120.7 (2)
C(3)–C(2)–P(1)	86.1 (1)	C(13)–C(12)–C(11)	120.9 (2)
C(5)–C(2)–P(1)	115.2 (2)	C(19)–C(13)–C(12)	120.7 (2)
C(5)–C(2)–C(3)	115.0 (2)	C(19)–C(14)–C(15)	120.8 (2)
C(6)–C(2)–P(1)	115.8 (2)	C(16)–C(15)–C(14)	119.7 (2)
C(6)–C(2)–C(3)	112.6 (2)	C(17)–C(16)–C(15)	121.2 (2)
C(6)–C(2)–C(5)	110.4 (2)	C(18)–C(17)–C(16)	120.9 (2)
C(4)–C(3)–C(2)	99.2 (2)	C(17)–C(18)–C(10)	122.8 (2)
C(7)–C(3)–C(2)	117.2 (2)	C(19)–C(18)–C(10)	119.4 (2)
C(7)–C(3)–C(4)	117.9 (2)	C(19)–C(18)–C(17)	117.8 (2)
C(3)–C(4)–P(1)	85.8 (1)	C(14)–C(19)–C(13)	121.8 (2)
C(8)–C(4)–P(1)	113.9 (2)	C(18)–C(19)–C(13)	118.8 (2)
C(8)–C(4)–C(3)	112.3 (2)	C(18)–C(19)–C(14)	119.4 (2)
C(9)–C(4)–P(1)	118.4 (2)		

A further observation by Fitzgerald *et al.* (1978) that the magnitude of puckering in unsymmetrically substituted phosphetanes is substantially larger than in symmetrically substituted compounds can probably now be discounted, based on subsequent studies. Thus, to date, the structures of twelve phosphetanes have been determined (Swank & Caughlan, 1968; Moret & Trefonas, 1969; Fitzgerald *et al.*, 1978; Mazhar-ul-Haque, 1970, 1971, 1979; Mazhar-ul-Haque, Horne, Cremer, Kremer & Kafarski, 1981; Mazhar-ul-Haque & Horne, 1982, 1984, unpublished results) with a mean puckering angle of  $24.5^\circ$  ( $\sigma = 5.1^\circ$ ).<sup>\*</sup> Seven of these are symmetrically substituted, with a mean puckering angle of  $23.7^\circ$  ( $\sigma = 4.0^\circ$ ) compared with a mean value of  $25.6^\circ$  ( $\sigma = 6.8^\circ$ ) for the unsymmetrically substituted ones.

The geometry around P in (I) is as expected in the presence of a four-membered ring. The internal angle at P is  $81.1(1)^\circ$  with adjacent angles  $86.1(1)$  and  $85.8(1)^\circ$ . The internal angle opposite to P is  $99.2(2)^\circ$ . These angles match very well with those found in other substituted phosphetanes. The naphthalene ring is essentially planar [with  $0.052(2)$  Å maximum deviation, r.m.s.d =  $0.035$  Å]. The P(1)–O(20) bond is relatively long, but consistent with values observed in other, similar structures (Swank & Caughlan, 1968; Mazhar-ul-Haque, 1970, 1971).

Other bond lengths and angles are comparable with the observed values in related structures (Mazhar-

ul-Haque, 1970, 1971). All non-hydrogen intermolecular contacts are larger than the sum of the van der Waals radii of the involved atoms.

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<sup>\*</sup> We have excluded from this analysis fused-ring phosphetanes such as, for example, the tetracyclic compound studied by Mazhar-ul-Haque, Rashid & Cremer (1978), due to the different ring constraints in these cases.

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## 10-Hydroxy-10-methyl-10,11-dihydroquinine, $C_{21}H_{28}N_2O_3$ , a New Derivative of Quinine

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**Abstract.**  $M_r = 356.5$ , orthorhombic,  $P2_12_12_1$ ,  $a = 11.199(3)$ ,  $b = 11.237(3)$ ,  $c = 15.318(4)$  Å,  $V = 1927.7(9)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.228$ ,  $D_m = 1.224(1)$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 0.077$  mm<sup>-1</sup>,  $F(000) = 768$ ,  $T = 293$  K, final  $R =$

$0.032$  for 1790 unique reflections. The molecular structure of the title compound is very similar to that of cinchonidine. The packing is determined by intermolecular hydrogen bonds between hydroxyl groups and N atoms of the quinuclidine moiety; this led to the formation of molecular layers parallel to the  $ab$  plane.

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