

acetoxy groups are less than 0.02 Å, and both acetoxy groups are attached to the C-atom rings in the usual eclipse form. There are no special intermolecular approaches to influence the molecular conformation significantly.

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Structure of 2,2-Dimethyl-1-phenyl- λ^3 -phosphetane 1-Oxide

BY MAZHAR-UL-HAQUE* AND WILLIAM HORNE

Department of Chemistry, University of Petroleum & Minerals, Dhahran, Saudi Arabia

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Abstract. $C_{11}H_{15}OP$, $M_r = 194.2$, monoclinic, space group $C2/c$, $Z = 8$, $a = 29.749$ (5), $b = 6.745$ (1), $c = 11.143$ (8) Å, $\beta = 107.33$ (2)°, $U = 2134.3$ Å³, $D_x = 1.21$ Mg m⁻³, $\mu(\text{Mo } K\alpha, \lambda = 0.71073 \text{ Å}) = 0.175$ mm⁻¹. The structure was solved by direct methods from diffractometer data and refined to an R value of 0.043 for 1374 observed reflections. The phosphetane ring is puckered with a dihedral angle of 25.8 (3)°.

Introduction. A number of previous X-ray structure studies on phosphetanes (Swank & Caughlin, 1968; Moret & Trefonas, 1969; Mazhar-ul-Haque, 1970, 1971, 1979; Fitzgerald, Campbell, Smith, Caughlin & Cremer, 1978) have indicated that these four-membered heterocyclic ring systems are significantly non-planar, with dihedral angles in the range 17–30° [exceptionally, one rigid and highly strained tetracyclic phosphetane (Mazhar-ul-Haque, Rashid & Cremer, 1978) did exhibit a dihedral angle of almost 47°].

The conformers which result from this ring non-planarity have provided an opportunity to investigate the stereochemical preferences of these systems. In

particular, Fitzgerald *et al.* (1978) correlated the preferred solid-state conformations with the extent and type of interactions between ring substituents. Additionally, these authors detected a qualitative correlation between the extent of ring substitution and the magnitude of the ring dihedral angle.

The present investigation is concerned with a structural study of a phosphetane with relatively little ring substitution.

Due to the hygroscopic nature of the crystals, no density measurement was attempted.

A crystal, *ca* 0.25 × 0.38 × 1.0 mm, mounted in a sealed glass capillary, was used for intensity measurements on an Enraf–Nonius CAD-4 diffractometer controlled by a PDP8/a computer at a take-off angle of 5° with graphite-monochromated Mo $K\alpha$ radiation.

Accurate cell dimensions and their standard deviations were obtained by least-squares refinement of the setting angles of 25 accurately centered reflections.

1874 independent reflections (to $\theta \leq 25^\circ$) were measured by ω - 2θ scans using the ZIGZAG routine (Enraf–Nonius, 1977); background counts were taken on each side of the peak. The intensities of three standard reflections were measured every 90 reflections and showed no significant change in intensities

* To whom correspondence should be addressed.

during data collection. A total of 1374 reflections were considered observed [$I > 3\sigma(I)$]. Lorentz and polarization corrections were applied as usual.

The structure was solved by direct methods with the automatic multiresolution routine of *SHELX 76* (Sheldrick, 1976). Full-matrix least-squares refinement with isotropic temperature factors gave $R = 0.106$ for the observed reflections; anisotropic temperature factors reduced R to 0.076. All the H atoms were located from a difference synthesis and further refinement of non-H atoms anisotropically and H atoms isotropically reduced R to 0.043. A weighting scheme based on counting statistics was used, with $w = [\sigma^2 |F_o| + 0.0046F_o^2]^{-1}$ minimizing $\sum w\Delta^2$. A final difference map showed a highest peak of $0.32 \text{ e } \text{\AA}^{-3}$.

Fig. 1 is an *ORTEP* drawing (Johnson, 1976) of the molecule illustrating 30% probability ellipsoids for the non-H atoms and arbitrary spheres of radius 0.1 \AA for the H atoms; Fig. 2 shows the packing arrangement.

Atomic positions for non-H atoms are listed in Table 1 and those for H atoms are in Table 2. Bond lengths

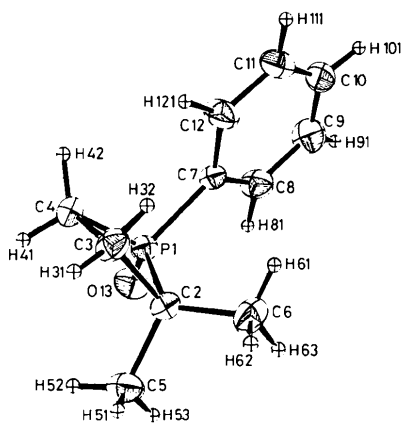


Fig. 1. View of 2,2-dimethyl-1-phenyl- λ^5 -phosphetane 1-oxide.

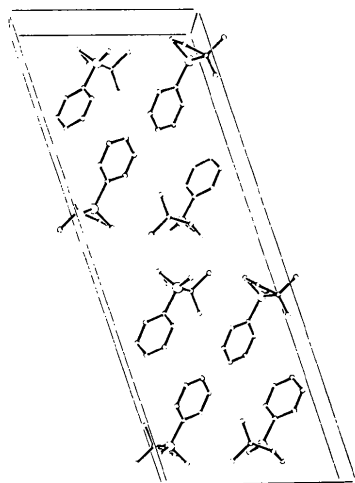


Fig. 2. The packing of the molecules.

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

$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
P(1)	842 (1)	4529 (1)	977 (1)	53
C(2)	862 (1)	2139 (3)	206 (2)	58
C(3)	673 (1)	1193 (4)	1232 (3)	70
C(4)	471 (1)	3079 (5)	1668 (3)	69
C(5)	488 (1)	2104 (5)	-1075 (3)	59
C(6)	1328 (1)	1356 (5)	116 (3)	100
C(7)	1403 (1)	4908 (4)	2168 (2)	52
C(8)	1690 (1)	6386 (4)	1997 (3)	74
C(9)	2131 (1)	6688 (6)	2846 (4)	70
C(10)	2285 (1)	5527 (6)	3889 (3)	60
C(11)	1997 (1)	4101 (6)	4099 (3)	90
C(12)	1557 (1)	3767 (5)	3264 (3)	76
O(13)	687 (1)	6360 (3)	234 (2)	81

Table 2. Fractional coordinates ($\times 10^3$) and isotropic temperature factors ($\text{\AA}^2 \times 10^3$) for H atoms with *e.s.d.*'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>	U_{iso}
H(31)	42 (1)	18 (5)	91 (3)	54 (7)
H(32)	94 (1)	62 (4)	188 (3)	51 (7)
H(41)	14 (1)	317 (4)	121 (3)	49 (7)
H(42)	53 (1)	327 (5)	261 (3)	76 (9)
H(51)	42 (1)	78 (5)	-127 (3)	74 (9)
H(52)	18 (1)	263 (5)	-110 (3)	76 (9)
H(53)	59 (1)	296 (5)	-163 (3)	83 (10)
H(61)	155 (1)	136 (5)	90 (4)	77 (10)
H(62)	127 (1)	-2 (6)	-18 (3)	81 (10)
H(63)	144 (2)	216 (7)	-50 (5)	140 (16)
H(81)	156 (1)	714 (5)	120 (3)	87 (10)
H(91)	232 (2)	774 (6)	273 (4)	102 (12)
H(101)	260 (1)	579 (6)	441 (4)	103 (13)
H(111)	210 (1)	314 (7)	482 (4)	124 (15)
H(121)	135 (1)	272 (4)	347 (3)	70 (19)

Table 3. Bond lengths (\AA) and angles ($^\circ$) with *e.s.d.*'s in parentheses

P(1)—C(2)	1.836 (2)	C(3)—C(4)	1.545 (4)
P(1)—C(4)	1.807 (3)	C(7)—C(8)	1.363 (4)
P(1)—C(7)	1.815 (2)	C(7)—C(12)	1.400 (4)
P(1)—O(13)	1.482 (2)	C(8)—C(9)	1.384 (4)
C(2)—C(3)	1.554 (3)	C(9)—C(10)	1.363 (5)
C(2)—C(5)	1.527 (4)	C(10)—C(11)	1.353 (5)
C(2)—C(6)	1.514 (4)	C(11)—C(12)	1.379 (4)
C(4)—P(1)—C(2)	80.4 (1)	C(6)—C(2)—C(5)	111.0 (2)
C(7)—P(1)—C(2)	108.3 (1)	C(4)—C(3)—C(2)	98.8 (2)
C(7)—P(1)—C(4)	108.0 (1)	C(3)—C(4)—P(1)	88.2 (2)
O(13)—P(1)—C(2)	121.2 (1)	C(8)—C(7)—P(1)	118.6 (2)
O(13)—P(1)—C(4)	124.1 (1)	C(12)—C(7)—P(1)	123.5 (2)
O(13)—P(1)—C(7)	110.9 (1)	C(12)—C(7)—C(8)	117.9 (2)
C(3)—C(2)—P(1)	86.9 (1)	C(9)—C(8)—C(7)	121.2 (3)
C(5)—C(2)—P(1)	109.6 (2)	C(10)—C(9)—C(8)	120.4 (3)
C(5)—C(2)—C(3)	111.0 (2)	C(11)—C(10)—C(9)	119.2 (3)
C(6)—C(2)—P(1)	119.7 (2)	C(11)—C(10)—C(7)	119.8 (3)
C(6)—C(2)—C(3)	116.4 (2)	C(12)—C(11)—C(10)	121.4 (3)

and angles involving non-H atoms are listed in Table 3.*

Discussion. Examination of intermolecular contacts less than 4.0 Å does not show any distances significantly less than the sum of the respective atomic van der Waals radii. As with other phosphetanes, the crystal packing is therefore somewhat loose and the effect of intermolecular forces on the molecular structure can be neglected.

In the following discussion the main structural features of the title compound (1) will be compared with those of two other unsymmetrically substituted phenylphosphetane oxides: 2,2,3-trimethyl-1-phenylphosphetane 1-oxide (compound 2) and 2,2,3,3,4-pentamethyl-1-phenylphosphetane 1-oxide (compound 3) (Fitzgerald *et al.*, 1978). The numbering schemes for these derivatives and their salient molecular dimensions are given in Fig. 3. The dihedral angle between the planes C(2)–P(1)–C(4) and C(2)–C(3)–C(4) is 25.8° (3) in compound (1), 16.7° in (2), and 29.8° in (3). In both (1) and (2), the phenyl group is pseudo-axial, whilst in (3) it adopts the pseudo-equatorial position.

Compounds (1) and (2) show no important differences in their equivalent bond lengths, whilst their shortened C(2)–C(3) and C(3)–C(4) distances compared with (3) indicate the relative paucity of ring-substituent interactions.

* Lists of structure factors, anisotropic thermal parameters and bond lengths and angles involving H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36972 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

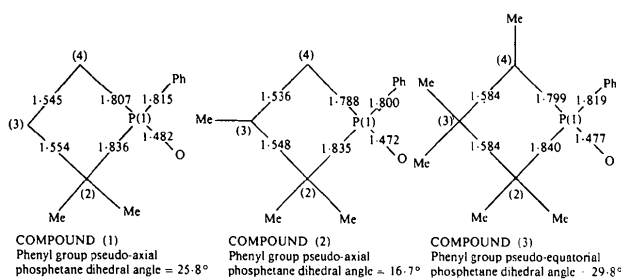


Fig. 3. Salient bond lengths (Å) and dihedral angles (°) for compounds (1)–(3).

The similarity in the molecular dimensions of (1) and (2) must be contrasted with their markedly different dihedral angles; in fact compound (1) has a dihedral angle which approaches the value attained in the highly ring-substituted compound (3). Geometrically, the large value of the dihedral angle in (1) is mainly related to the significant decrease (*ca* 3°) in the angle P(1)–C(2)–C(3) compared with the corresponding value in compound (2).^{*} No plausible explanation for this effect in terms of the extent of ring substitution is, however, apparent.

On the basis of the present results, therefore, it appears that qualitative correlations between dihedral angle and extent of ring substitution in phosphetanes must be viewed with some caution.

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* The dihedral angle in four-membered rings is highly sensitive to quite small changes in ring angles. For example, Dunitz (1979) has pointed out that for an equilateral, equiangular system, a change in ring angle from 90 to 89° results in a 22° change in puckering (dihedral) angle.

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