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## 1-Benzyl-2-phenyl-3-hydroxy-4,5-dimethylphosphol-2-ene 1-Oxide

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**Abstract.**  $C_{19}H_{21}O_2P$ , m.p. 181–183°, orthorhombic, space group  $Pc2_1b$ ,  $a=8.1319$  (6),  $b=8.5671$  (7),  $c=24.081$  (3) Å,  $Z=4$ ,  $M=312.33$ ,  $D_x=1.236$ ,  $D_m=1.236$  g cm<sup>-3</sup>. The title compound exists in the enol form having a C(2)–C(3) bond length of 1.357 Å. The stereochemistry at P and C(5) is *trans* as is the stereochemistry at C(4) and C(5). A strong hydrogen bond is formed between the P=O and O–H related by the twofold screw axis.

**Introduction.** The title compound represents a novel class of 2-phospholene-3-ole structures which may serve as starting materials for C–P heterocycles with possible biological activity. Certain phospholenes have shown biological activity [Vizel, Zvereva, Ivanovskaya, Studentsova, Dunaev & Berim (1965); Arbuzav, Vizel, Zvereva, Studentsova & Garaev (1966)] and the fact that alkylation appears to be sterically influenced (Purdum & Berlin, 1974) should stimulate interest. A preliminary report of this structure has been published (Washecheck, van der Helm, Purdum & Berlin, 1975).

The compound was recrystallized from ethanol–water mixture. A prismatic crystal, approximately 0.5 × 0.3 × 0.15 mm, was used for data collection and unit-cell determination. The unit-cell dimensions were determined at 27°C from the +2 $\theta$  and –2 $\theta$  values of 30 reflections distributed through all octants of recip-

rocal space. The data showed definite systematic absences of 0k0,  $k=2n+1$  and 00l,  $l=2n+1$  with very weak or zero intensities, and inconsistent from crystal to crystal for  $hk0$ ,  $k=2n+1$  and  $0kl$ ,  $l=2n+1$  indicating a probable space group of  $Pc2_1b$ ,  $Pcmb$  or  $P22_12_1$ . Space group  $Pc2_1b$  was later confirmed by the structure solution when an attempted refinement in space group  $P22_12_1$  failed. The intensities of 1852 reflections [1766 reflections had  $I > 2\sigma(I)$ ] with  $2\theta < 150^\circ$  were measured using Cu  $K\alpha$  radiation ( $\lambda=1.5418$  Å) and  $\theta$ – $2\theta$  scans on a Nonius CAD-4 automatic diffractometer. Absorption corrections ( $\mu=14.7$  cm<sup>-1</sup>) and Lorentz and polarization corrections were applied. The program used for the absorption corrections was that of Coppens, Leiserowitz & Rabinovich (1965) and employs the method of Gaussian integration. In this case 216 sampling points were used and the correction factor ranged from 0.5779 to 0.8245.

The structure was solved using conventional Patterson and Fourier techniques. The hydrogen atoms were located in a difference Fourier map based on the refined positions of the P, O and C atoms. The structure was refined using block-diagonal least-squares techniques (Ahmed, 1966) with anisotropic temperature factors for the non-hydrogen atoms and isotropic temperature factors for the hydrogen atoms. The refinement was terminated when all shifts for the non-hydrogen atoms were less than 0.6 of the corresponding estimated standard deviation. The error in an observation of unit weight,  $[\sum w(F_o - F_c)^2 / (m - n)]^{1/2}$ , where  $m$  = the number

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of observations and  $n$  = the number of parameters, is 1.42. Scattering factors for P, O and C atoms were taken from *International Tables for X-ray Crystallography* (1962) and those for H atoms from Stewart, Davidson & Simpson (1965). The  $R$  value for all data based on the final parameters (Tables 1 and 2) was 0.035.\* The weights of  $F$  in the least-squares calculations were calculated from  $\sigma(I)$  which were determined from counting statistics (van der Helm, Ealick & Burks, 1975). A final analysis of the structure factors does not show a significant variation of  $w\Delta F^2$  with either  $F_o$  or  $\sin \theta/\lambda$ .

**Discussion.** An ORTEP drawing of a single molecule is given in Fig. 1, bond lengths in Fig. 2 and bond angles

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31460 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Positional parameters* ( $\times 10^3$ ) and *isotropic thermal parameters* ( $\text{\AA}^2$ ) for hydrogen atoms

	$x$	$y$	$z$	$B$
H(C4)	433 (3)	-26 (4)	-19 (1)	4.1 (6)
H(C5)	120 (4)	9 (4)	27 (1)	5.6 (7)
H(C4a)A	483 (3)	-212 (4)	53 (1)	4.3 (6)
H(C4a)B	301 (3)	-244 (5)	23 (1)	6.0 (7)
H(C4a)C	318 (4)	-148 (5)	80 (1)	6.4 (8)
H(C5a)A	171 (4)	0 (5)	-68 (1)	7.4 (9)
H(C5a)B	255 (4)	191 (5)	-60 (1)	7.1 (10)
H(C5a)C	55 (4)	144 (5)	-50 (1)	5.0 (9)
H(C11)A	115 (3)	345 (3)	138 (1)	4.3 (6)
H(C11)B	-20 (3)	255 (4)	98 (1)	4.8 (6)
H(C13)	-102 (3)	-9 (4)	112 (1)	4.4 (6)
H(C14)	-81 (3)	-230 (4)	156 (1)	5.8 (7)
H(C15)	123 (3)	-310 (3)	220 (1)	4.1 (6)
H(C16)	324 (3)	-112 (4)	241 (1)	6.2 (7)
H(C17)	313 (3)	132 (4)	191 (1)	4.9 (6)
H(C22)	360 (5)	522 (6)	111 (2)	8.9 (10)
H(C23)	499 (4)	660 (4)	170 (1)	6.9 (9)
H(C24)	731 (4)	555 (5)	232 (2)	8.3 (10)
H(C25)	830 (4)	308 (5)	216 (1)	7.4 (10)
H(C26)	682 (3)	163 (4)	149 (1)	4.8 (6)
H(O3)	692 (4)	-19 (5)	25 (1)	7.2 (9)

Table 1. *Positional parameters* ( $x \times 10^4$ ,  $y \times 10^4$ ,  $z \times 10^5$ ) and *isotropic thermal parameters* ( $\times 10^4$ ) for P, C and O atoms

The standard deviation for last digit is in parentheses. Thermal parameters are of the form:

$$\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + \dots + 2U_{23}klb^*c^*)].$$

	$x$	$y$	$z$	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
P	2346.7 (6)	2524.1 (11)	5661 (2)	369 (2)	353 (2)	444 (3)	62 (3)	68 (2)	85 (3)
C(2)	4375 (3)	2182 (3)	8107 (9)	414 (10)	351 (12)	397 (9)	33 (9)	41 (8)	10 (8)
C(3)	4988 (3)	921 (3)	5395 (8)	406 (10)	373 (11)	397 (9)	48 (9)	9 (8)	22 (9)
C(4)	3840 (3)	-71 (3)	1993 (9)	457 (11)	399 (12)	408 (9)	24 (10)	24 (9)	-41 (10)
C(5)	2158 (3)	768 (3)	1438 (10)	406 (11)	476 (14)	479 (12)	-22 (11)	-7 (9)	47 (11)
C(4a)	3648 (4)	-1672 (3)	4772 (12)	695 (16)	373 (15)	658 (15)	27 (14)	97 (13)	-20 (11)
C(5a)	1662 (4)	1128 (5)	-4549 (11)	567 (15)	792 (23)	543 (15)	-27 (16)	-110 (12)	48 (15)
C(11)	906 (3)	2413 (4)	11427 (11)	519 (12)	490 (15)	629 (15)	133 (13)	205 (10)	127 (15)
C(12)	1004 (3)	877 (3)	14575 (9)	451 (11)	444 (13)	411 (9)	75 (10)	121 (9)	56 (10)
C(13)	-128 (3)	-286 (4)	13626 (10)	449 (12)	644 (17)	508 (12)	-33 (13)	-18 (10)	123 (13)
C(14)	-26 (4)	-1702 (4)	16376 (12)	710 (17)	584 (16)	543 (15)	-166 (16)	-14 (12)	96 (14)
C(15)	1214 (4)	-1965 (4)	20103 (13)	901 (20)	569 (17)	523 (15)	-25 (16)	-63 (14)	129 (13)
C(16)	2350 (4)	-805 (4)	21162 (11)	708 (16)	711 (20)	435 (12)	32 (16)	-90 (11)	79 (14)
C(17)	2255 (3)	607 (4)	18410 (9)	545 (13)	569 (16)	408 (12)	-53 (13)	27 (9)	-54 (11)
C(21)	5209 (3)	3181 (3)	12243 (9)	483 (11)	386 (11)	405 (12)	-25 (10)	115 (9)	-24 (9)
C(22)	4677 (4)	4716 (3)	13160 (11)	689 (16)	411 (13)	590 (15)	4 (13)	144 (13)	-60 (11)
C(23)	5423 (5)	5632 (4)	17192 (13)	1081 (27)	480 (17)	726 (18)	-73 (18)	236 (18)	-223 (16)
C(24)	6691 (5)	5055 (5)	20323 (12)	1037 (25)	715 (22)	538 (15)	-320 (20)	106 (16)	-222 (16)
C(25)	7240 (4)	3541 (4)	19478 (12)	724 (17)	761 (22)	520 (15)	-195 (17)	-26 (13)	-78 (15)
C(26)	6492 (3)	2632 (4)	15480 (10)	575 (13)	473 (14)	473 (12)	-24 (14)	1 (9)	-40 (13)
O(1)	2117 (2)	4039 (3)	2595 (8)	492 (9)	470 (10)	614 (9)	97 (9)	97 (7)	192 (9)
O(3)	6563 (2)	486 (2)	5756 (7)	434 (8)	575 (12)	514 (9)	155 (8)	-62 (7)	-134 (8)

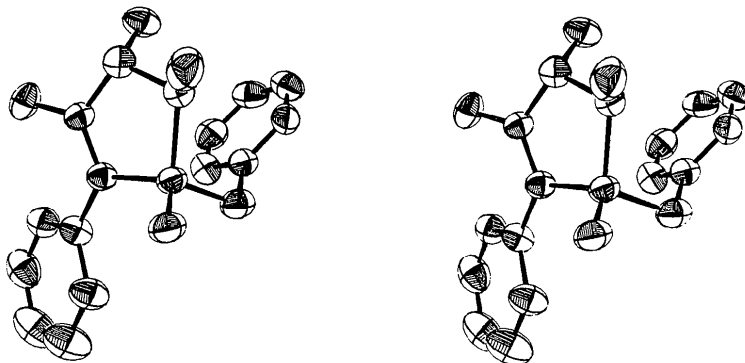


Fig. 1. Stereo view of a single molecule (Johnson, 1965).

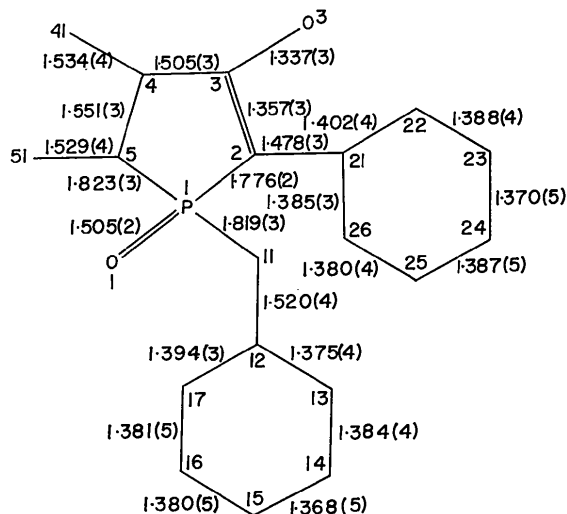


Fig. 2. Bond distances and numbering scheme.

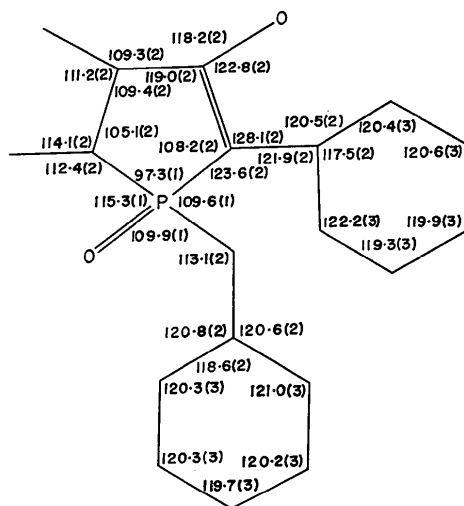


Fig. 3. Bond angles. Additional bond angles are C(2)–P(1)–O(1) = 114.9 (1) and C(5)–P(1)–C(11) = 109.2 (1)°.

in Fig. 3. The range of C–H bond lengths is 0.84 to 1.11 Å with an average value of 1.00 Å. The fact that the molecule exists in the enol form is evident in the C(2)–C(3) bond distance of 1.357 (3) Å, which is very close to the value expected for a double bond, location of a hydrogen atom bonded to O(3) and the fact that the sums of the bond angles about C(2) and C(3) are each 360.0° indicating  $sp^2$  hybridized atoms. The slight lengthening of the double bond may be correlated with an average deviation of the torsion angles about the C(2)–C(3) bond of 9.1° from the expected values for a planar double bond. The phenyl group attached to C(2) is not coplanar with the phospholene ring but is tilted away from atom O(3) as indicated by the torsion angle P(1)–C(2)–C(21)–C(26) = 156.9°. This results from a close intramolecular contact of 2.423 Å between O(3) and H(C26). The repulsion resulting from this contact may also be responsible for the non-planarity of the double-bond system. The attachment of the

Table 3. Least-squares plane through the phospholene ring and distances from the plane

Equation of the plane is:  $2.644x + 4.443y - 19.041z = 0.638$ , where  $x$ ,  $y$ , and  $z$  are fractional coordinates.

	$d(\text{Å})$		$d(\text{Å})$
P(1)	0.026	C(5)	0.000
C(2)	-0.055	*O(3)	0.217
C(3)	0.063	*C(21)	-0.179
C(4)	-0.034		

\* Not included in calculation of least-squares plane.

benzyl group is staggered with respect to P=O as can be seen by the value of 177.2 for the torsion angle O(1)–P(1)–C(11)–C(12). The attachment of the benzene ring to atom C(11) is tilted from perpendicular by 11.4°. The stereochemistry of the methyl groups attached to C(4) and C(5) is *trans* and that of methyl group C(5) and the benzyl group is also *trans*. Torsion angles in the phospholene rings are  $\varphi_1 = 7.3^\circ$ ,  $\varphi_2 = -11.4^\circ$ ,  $\varphi_3 = 10.4^\circ$ ,  $\varphi_4 = -3.8^\circ$  and  $\varphi_5 = -1.7^\circ$  where  $\varphi_i$  is the interior torsion angle about the bond joining atoms  $i$  and  $i + 1$ . The equation of a least-squares plane passing through the five-membered ring and distances of several atoms from that plane are given in Table 3. The near-planarity of the phospholene ring can be seen and the non-planarity of the double bond is also evident.

The –OH group on C(3) is involved in a strong hydrogen bond, joining symmetry-related molecules about the twofold screw axis. The O(1)⋯O(3) distance is 2.595 Å, O(3)–H(O3) is 1.03(4) Å, the O(1)⋯H(O3) distance is 1.590 Å and the O(1)⋯H(O3)–O(3) angle is 165.5° [atoms H(O3) and O(3) are transformed by  $1 - x, \frac{1}{2} + y, -z$ ].

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