

## Conformation of the 2-Phospholene Ring. The Structure of 4-Hydroxy-1-phenyl-2-phospholene 1-Oxide

BY Z. GALDECKI AND M. L. GŁÓWKA

*Institute of General Chemistry, Technical University of Łódź, Żwirki 36, 90–924 Łódź, Poland*

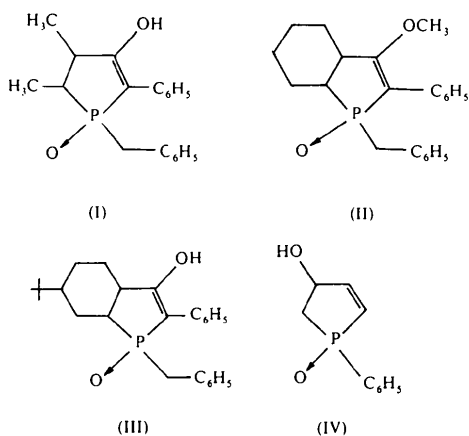
(Received 9 May 1979; accepted 24 December 1979)

**Abstract.**  $C_{10}H_{11}O_2P$ ,  $M_r = 194.17$ ,  $F(000) = 408$ , orthorhombic,  $P2_12_12_1$ ,  $a = 10.246(3)$ ,  $b = 9.416(3)$ ,  $c = 9.978(3)$  Å,  $V = 964.64$  Å<sup>3</sup>,  $Z = 4$ .  $D_m = 1.32$ ,  $D_x = 1.339$  Mg m<sup>-3</sup>,  $\mu(\text{Cu } K\alpha) = 2.22$  mm<sup>-1</sup>. The structure was solved by direct methods, and refined by full-matrix least squares to  $R = 0.037$  for 779 reflections. Hydrogen bonds connect the molecules in chains parallel to the  $x$  axis (O...O distance 2.716 Å). The phospholene ring is flattened and has a conformation intermediate between C(5) sofa and C(2) half-chair with asymmetry parameters:  $\Delta C_5^s = 2.6(2)$ ,  $\Delta C_2^s = 3.7(2)$ ,  $\varphi = 8.0(2)^\circ$ . The configurations of the asymmetric atoms P(1) and C(4) are opposite. The plane of the benzene ring is perpendicular to that of the phospholene ring. An extremely short (1.305 Å) double bond is observed.

**Introduction.** The present study is a continuation of our investigation of the structure and conformation of the phospholene ring. Up to now, only three related structures have been determined by X-ray analysis. Washecheck, van der Helm, Purdum & Berlin (1974) have published the results of their crystallographic studies of 1-benzyl-3-hydroxy-4,5-dimethyl-2-phenyl-2-phospholene 1-oxide (I) in the form of a very short, incomplete communication. The structures of two other compounds, 7-benzyl-9-methoxy-8-phenyl-7-phosphabicyclo[4.3.0]non-8-ene 7-oxide (II) and its 4-*tert*-

butyl-9-hydroxy analogue (III), have been examined by the present authors (Galdecki, 1979; Galdecki & Głowska, 1980). The assignment of the relative configuration at P(1) and C(4) would prove helpful for the determination of the stereochemistry of the stereospecific reaction in which the molecule was formed (Bodalski & Janecki, 1977).

Colourless, transparent crystals of the compound were crystallized from ethyl acetate. 779 independent reflections were collected on a Syntex  $P2_1$  diffractometer from a crystal shaped into a sphere of diameter about 0.3 mm (Cu  $K\alpha$  radiation); 758 reflections with  $F_o \geq 2\sigma(F_o)$  were assumed to be observed. The density of the crystals was determined by flotation. Intensities of two systematically absent reflections, 010 and 300, were relatively high ( $\approx 15\sigma$ ), probably due to a Renninger effect. The phases of  $200 E \geq 1.36$  were determined with *MULTAN* (Germain, Main & Woolfson, 1971). The second of the solutions gave the positions of five atoms and a further Fourier synthesis revealed the whole molecule ( $R = 0.213$ ). This model of the molecule was refined by full-matrix least squares using the *CRYLSQ* program of the XRAY 70 system (Stewart, Kundell & Baldwin, 1970). Refinement was initially performed with unit weights (four cycles, isotropic) and then with the weighting scheme  $w = [\sigma(F)]^{-2}$ . Three cycles of refinement with isotropic and then two with anisotropic thermal parameters led to  $R = 0.067$  and  $R_w = 0.084$ . At this stage the H atoms were found from a difference Fourier map and all the atoms of the molecule were refined in five cycles (H with isotropic, other atoms with anisotropic temperature factors). The final conventional  $R$  factor was 0.037 ( $R_w = 0.041$ ) excluding unobserved reflections.\* The scattering factors for P, O and C were those of Doyle & Turner (1968) and for H those in *International Tables for X-ray Crystallography* (1962). The calculations were carried out on ODR-1305 (*MULTAN*) and RIAD 32 computers.



\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35001 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Atomic parameters are given in Tables 1 and 2. Bond lengths and angles are in Table 3.

**Discussion.** The molecule and atom-numbering system are shown in Fig. 1. The most significant feature of the phospholene ring is its planarity. The mean torsional angle is  $8.0(2)^\circ$  and distances of the atoms from the

Table 1. Positions ( $\times 10^4$ ) and isotropic temperature factors for non-hydrogen atoms with their *e.s.d.*'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>iso</sub> (Å <sup>2</sup> )
P(1)	7872 (1)	2305 (1)	5685 (1)	3.5 (1)
O(1)	6838 (3)	1210 (3)	5833 (4)	4.6 (2)
O(2)	9632 (4)	4079 (6)	2682 (4)	6.7 (2)
C(2)	7332 (5)	4056 (6)	5271 (6)	4.8 (3)
C(3)	7741 (6)	4439 (6)	4087 (6)	5.7 (3)
C(4)	8540 (3)	3402 (7)	3280 (5)	5.2 (3)
C(5)	8885 (5)	2143 (7)	4197 (7)	5.0 (3)
C(11)	8835 (4)	2438 (5)	7183 (4)	3.1 (2)
C(12)	8451 (5)	1700 (5)	8327 (5)	3.8 (2)
C(13)	9149 (6)	1838 (6)	9501 (5)	5.2 (3)
C(14)	10226 (5)	2704 (6)	9560 (6)	4.8 (3)
C(15)	10607 (5)	3435 (6)	8441 (6)	4.7 (3)
C(16)	9937 (5)	3300 (5)	7251 (5)	4.1 (2)

Table 2. Final atomic parameters ( $\times 10^3$ ) for H atoms and H—C (H—O) bond lengths (Å)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>iso</sub> (Å <sup>2</sup> )	Bonded to	Bond length (Å)
H(1)	1023 (6)	401 (7)	325 (6)	4 (2)	O(2)	0.84 (6)
H(2)	670 (6)	472 (6)	586 (6)	5 (2)	C(2)	1.07 (6)
H(3)	764 (7)	552 (6)	369 (7)	6 (2)	C(3)	1.09 (7)
H(4)	806 (5)	312 (5)	251 (4)	2 (1)	C(4)	0.95 (5)
H(51)	894 (4)	118 (5)	404 (4)	1 (1)	C(5)	0.92 (4)
H(52)	987 (6)	217 (6)	447 (5)	5 (1)	C(5)	1.04 (6)
H(12)	774 (5)	107 (5)	829 (4)	2 (1)	C(12)	0.94 (5)
H(13)	886 (4)	140 (4)	1025 (4)	1 (1)	C(13)	0.90 (4)
H(14)	1077 (4)	270 (5)	1031 (5)	2 (1)	C(14)	0.93 (5)
H(15)	1133 (4)	397 (4)	845 (4)	1 (1)	C(15)	0.90 (4)
H(16)	1012 (4)	381 (5)	657 (4)	1 (1)	C(16)	0.85 (4)

Table 3. Bond lengths (Å) and angles ( $^\circ$ )

P(1)—O(1)	1.486 (3)	O(1)—P(1)—C(2)	116.3 (2)
P(1)—C(2)	1.787 (5)	O(1)—P(1)—C(5)	115.5 (3)
P(1)—C(5)	1.818 (6)	O(1)—P(1)—C(11)	110.9 (2)
P(1)—C(11)	1.795 (4)	C(2)—P(1)—C(5)	93.8 (3)
C(2)—C(3)	1.305 (8)	C(2)—P(1)—C(11)	107.3 (2)
C(3)—C(4)	1.508 (8)	C(5)—P(1)—C(11)	111.9 (2)
C(4)—C(5)	1.539 (9)	P(1)—C(2)—C(3)	111.4 (4)
C(4)—O(2)	1.420 (7)	P(1)—C(5)—C(4)	106.8 (4)
C(11)—C(12)	1.393 (7)	C(2)—C(3)—C(4)	118.6 (5)
C(12)—C(13)	1.378 (8)	C(3)—C(4)—C(5)	107.9 (5)
C(13)—C(14)	1.373 (8)	C(3)—C(4)—O(2)	111.2 (5)
C(14)—C(15)	1.368 (8)	C(5)—C(4)—O(2)	114.5 (5)
C(15)—C(16)	1.378 (8)	P(1)—C(11)—C(12)	119.5 (3)
C(16)—C(11)	1.392 (7)	P(1)—C(11)—C(16)	121.8 (4)
O(1)⋯H(1)	1.89 (6)	C(11)—C(12)—C(13)	120.2 (5)
O(2)—H(1)⋯O(1)	167 (6)	C(12)—C(13)—C(14)	120.6 (5)
C(4)—O(2)—H(1)	105 (4)	C(13)—C(14)—C(15)	119.5 (5)
		C(14)—C(15)—C(16)	121.0 (5)
		C(15)—C(16)—C(11)	120.0 (5)
		C(16)—C(11)—C(12)	118.6 (4)

least-squares plane through P(1), C(2) to C(5) are not greater than  $0.09 \text{ \AA}$ , while in other structures containing a phospholene ring (Table 4) those values are about  $20^\circ$  and about  $0.22 \text{ \AA}$  respectively. The conformation of the ring is intermediate between C(5) sofa and C(2) half-chair, as was the case in (II) (Gałdecki, 1979). Unexpectedly, the conformation of the phospholene ring in the 9-hydroxy-4-*tert*-butyl analogue (III) of the bicyclic compound is different; it is pure C(2) envelope. The asymmetry parameters (Duax & Norton, 1975) for these three compounds are given in Table 4. The asymmetry parameters for (I) are not included in the table as they could not be calculated, since neither

Table 4. Comparison of some structural parameters for known compounds containing the 2-phospholene ring

	(I) Washecheck <i>et al.</i> (1974)	(II) Gałdecki (1979)	(III) Gałdecki & Główska (1980)	(IV) Present study
Bond lengths (Å)				
P(1)—O(1)	1.506	1.492 (8)	1.501 (3)	1.486 (3)
P(1)—C(2)	1.776	1.788 (11)	1.778 (3)	1.787 (5)
P(1)—C(5)	1.822	1.814 (12)	1.814 (3)	1.818 (6)
P(1)—Bz(Ph)	1.819	1.823 (11)	1.816 (3)	1.795 (4)
C(2)—C(3)	1.356	1.330 (15)	1.354 (4)	1.305 (8)
C(3)—C(4)	1.505	1.530 (15)	1.515 (4)	1.508 (8)
C(4)—C(5)	1.551	1.526 (16)	1.548 (4)	1.539 (9)
C—O	1.337	1.376 (12)	1.336 (2)	1.420 (7)
Valency angles ( $^\circ$ )				
C(2)—P(1)—C(5)		94.1 (5)	93.7 (1)	93.8 (3)
P(1)—C(2)—C(3)	108.2	107.8 (8)	108.1 (2)	111.4 (4)
C(2)—C(3)—C(4)	118.9	119.1 (9)	117.7 (2)	118.6 (5)
C(3)—C(4)—C(5)		104.6 (9)	105.4 (2)	107.8 (5)
C(4)—C(5)—P(1)		104.6 (7)	102.8 (2)	106.8 (4)
O(1)—P(1)—C(2)		116.5 (4)	116.5 (1)	116.3 (2)
O(1)—P(1)—C(5)		118.7 (4)	118.6 (1)	115.5 (3)
O(1)—P(1)—Bz(Ph)		111.9 (5)	106.9 (1)	110.9 (2)
Torsional angles ( $^\circ$ )				
P(1)—C(2)—C(3)—C(4)	8.0	2.8 (5)	1.6 (2)	1.1 (3)
Asymmetry parameters ( $^\circ$ )				
$\Delta C_1^2$		6.3 (4)	1.6 (2)	2.6 (2)
$\Delta C_2^2$		9.2 (4)	17.5 (2)	3.7 (2)
$\Delta C_3^2$		18.3 (4)	16.8 (2)	7.4 (2)
$\phi$		19.9 (4)	22.0 (2)	8.0 (2)

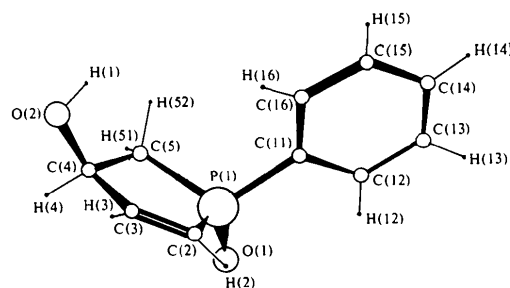


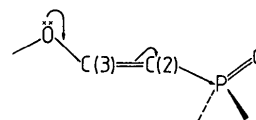
Fig. 1. View of the molecule along [010] and numbering system of atoms.

atomic parameters nor torsional angles are mentioned in the paper of Washecheck *et al.* (1974).

The benzene ring is nearly perpendicular to the phospholene ring. The angle between least-squares planes calculated for the rings is  $88.6(3)^\circ$ . The valency angles in the benzene ring are close to the normal value within limits of error. That  $C(16)-C(11)-C(12)$  is significantly less than  $120^\circ$  is in accord with a well known effect (Domenicano, Vaciago & Coulson, 1975). The configurations of both the asymmetric atoms P(1) and C(4) are opposite in the Cahn-Ingold-Prelog notation (Cahn, Ingold & Prelog, 1956).

The packing of the molecules of 4-hydroxy-1-phenyl-2-phospholene 1-oxide is shown in Fig. 2. The molecules form chains by means of intermolecular hydrogen bonds between the phosphoryl O atoms and the 4-hydroxy groups along 2<sub>1</sub> axes in the [100] direction. The chains are well separated. There are no intermolecular contacts shorter than the sums of the van der Waals radii.

Besides the flattening of the phospholene ring in the examined structure, a very short  $C(2)=C(3)$  bond ( $1.305 \text{ \AA}$ ) is observed. We assume that elongation of the bond in other compounds examined by X-ray methods to about  $1.35 \text{ \AA}$  (Table 4) is caused by conjugation of the lone electron pair of the O atom at the 3 position with the double-bond system.



The elongation of the  $C(4)-O$  bond in the title compound (IV) to  $1.420 \text{ \AA}$ , compared to about  $1.35 \text{ \AA}$  for the  $C(3)-O$  bonds in the other 2-phospholene 1-oxide derivatives studied, confirms the conjugation (Table 4). Increase of the valency angle  $P(1)-C(2)=C(3)$  in this structure from  $108$  to  $111.4^\circ$ , *i.e.* approximating the  $120^\circ$  normal for  $C(sp^2)$ , also indicates conjugation. Other differences in bond lengths and angles of comparable compounds are smaller and refer to the  $C(3)-C(4)-C(5)$  and  $C(4)-C(5)-P(1)$  angles which are  $2$  to  $4^\circ$  greater in the present structure because of the absence of a fused cyclohexane ring. However, the equalization of the valence angles  $O(1)-P(1)-C(2)$  and  $O(1)-P(1)-C(5)$  (the difference is  $0.8^\circ$  in the present structure and about  $2^\circ$  in bicyclic compounds) results from the flattening of the phospholene ring.

The authors are indebted to Professor R. Bodalski and Mr T. Janecki for pointing out the interesting features of this material and for supplying the crystals. This research was supported by project MR.I-9 from the Polish Academy of Sciences.

#### References

- BODALSKI, R. & JANECKI, T. (1977). Private communication.
- CAHN, R. S., INGOLD, C. K. & PRELOG, V. (1956). *Experientia*, **12**, 81-94.
- DOMENICANO, A., VACIAGO, A. & COULSON, C. A. (1975). *Acta Cryst. B* **31**, 221-234, 1630-1641.
- DOYLE, P. A. & TURNER, P. S. (1968). *Acta Cryst. A* **24**, 390-397.
- DUAX, W. L. & NORTON, D. A. (1975). *Atlas of Steroid Structure*, pp. 16-22. New York: Plenum.
- GALDECKI, Z. (1979). *Acta Cryst. B* **35**, 2225-2227.
- GALDECKI, Z. & GŁÓWKA, M. L. (1980). *Acta Cryst.* To be published.
- GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst. A* **27**, 368-376.
- International Tables for X-ray Crystallography* (1962). Vol. III, pp. 202-203. Birmingham: Kynoch Press.
- STEWART, J. M., KUNDELL, P. A. & BALDWIN, J. C. (1970). The XRAY 70 system. Computer Science Center, Univ. of Maryland, College Park, Maryland.
- WASHECHECK, D. M., VAN DER HELM, D., PURDUM, W. R. & BERLIN, K. D. (1974). *J. Org. Chem.* **39**, 3305-3307.

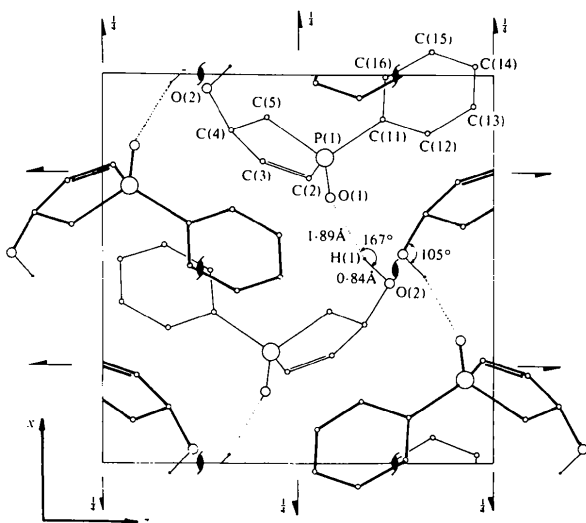


Fig. 2. Packing of molecules in the unit cell and hydrogen bonding.