The Structure of 2-Hydroxy-2-methyl-1-phenylphospholane 1-Oxide

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Abstract. $C_{11}H_{15}O_2P$, $M_r = 210 \cdot 2$, monoclinic, $P2_1/c$, $a = 9 \cdot 913$ (2), $b = 12 \cdot 046$ (3), $c = 10 \cdot 125$ (2) Å, $\beta = 115 \cdot 82$ (3)°, $V = 1088 \cdot 3$ Å^3, $Z = 4$, D_m (flotation) $= 1 \cdot 274$, $D_c = 1 \cdot 283$ Mg m^{-3}, μ(Cu $K\alpha$) $= 1 \cdot 56$ mm^{-1}. The structure was solved by direct methods and refined by least squares to a final R of $0 \cdot 050$ ($R_w = 0 \cdot 048$) for 1703 intensities. Dimeric molecules are formed in the crystal by means of hydrogen bonds with an $O \cdots O$ distance of $2 \cdot 70$ Å. The phospholane ring is in a nearly ideal sofa conformation with $\Delta C_s^{\min} = 1 \cdot 9$ (3)°.

Introduction. The present study is a continuation of our investigations of the crystal structures of compounds containing a phospholane or phospholene ring. The study was started with two aims: to compare the conformations of P-containing five-membered rings in the absence of an unsaturated bond, and to assign relative configurations at the P and C(2) atoms to elucidate the mechanism of molecule formation. Several compounds related structurally to this phospholane oxide have been studied by Alver & Kjøge (1969). The phospholene ring exists in compounds reported by Washecheck, Helm, Purdum & Berlin (1974) and by ourselves (Gałdecki, 1979; Gałdecki & Główka, 1980); the compounds are 1-benzyl-3-hydroxy-4,5-dimethyl-2-phenylphosphol-2-ene 1-oxide, 7-benzyl-9-methoxy-8-phenyl-7-phosphabicyclo[4.3.0]non-8-ene 7-oxide and 7-benzyl-4-*tert*-butyl-9-hydroxy-8-phenyl-7-phosphabicyclo[4.3.0]non-8-ene 7-oxide, respectively.

Colourless, prismatic crystals suitable for X-ray studies were kindly provided by Dr Waszkuć. Accurate unit-cell dimensions were determined on a diffractometer.

A crystal, approximately 0·3 mm in diameter, was used for the data collection. Intensities were recorded by the θ–2θ scan technique on a CAD-4 four-circle single-crystal diffractometer with Cu radiation. The total number of independent reflections measured was 1703. Intensities were not corrected for absorption. The scattering factors used were those given by Doyle & Turner (1968) for P, O and C and those from *International Tables for X-ray Crystallography* (1962) for H.

The structure was solved by the symbolic-addition procedure. Of 349 $E \geq 1 \cdot 3$ the signs of 214 (102 + and 112 −) have been determined by the program *PHASE* of the XRAY 70 system (Stewart, Kundell & Baldwin, 1970). The resultant E map showed the positions of 13 atoms ($R = 33 \cdot 7\%$) and a subsequent Fourier synthesis revealed the remaining non-hydrogen atoms.

Full-matrix least-squares refinement (*CRYLSQ*) of this model resulted in $R = 0 \cdot 095$ after six cycles with isotropic ($R = 0 \cdot 126$) and a further three cycles with anisotropic thermal parameters. A difference map revealed the sites for all the H atoms, which were refined in two cycles with isotropic temperature factors ($R = 0 \cdot 077$). The final agreement factors were $R = 0 \cdot 050$ and $R_w = 0 \cdot 048$ after five more cycles of block-diagonal refinement of all the atoms (H with isotropic and other atoms with anisotropic temperature factors) excluding 303 'less-than' reflections with $|F_o| \leq 3\sigma(F_o)$. The weighting scheme applied was $w = [\sigma(F)]^{-2}$. Final atomic parameters together with their standard deviations as obtained from the refinement are given in Tables 1 and 2.* All calculations were processed using the XRAY 70 system (Stewart, Kundell & Baldwin, 1970) on a RIAD 32 computer.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35295 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional parameters* ($\times 10^4$) *and isotropic thermal parameters for the non-hydrogen atoms*

	x	y	z	B_{iso} (Å^2)
P(1)	6458 (1)	3739 (1)	1470 (1)	2·3 (1)
O(1)	6616 (3)	4402 (2)	296 (2)	3·0 (1)
O(2)	5694 (3)	5594 (2)	2414 (3)	3·8 (1)
C(2)	6397 (4)	4554 (3)	2993 (4)	3·1 (1)
C(3)	5387 (5)	3842 (4)	3428 (5)	3·8 (2)
C(4)	4069 (5)	3434 (4)	2029 (5)	3·8 (2)
C(5)	4682 (4)	3036 (3)	948 (5)	3·1 (1)
C(11)	7962 (4)	2742 (3)	2235 (4)	2·8 (1)
C(12)	7846 (5)	1761 (3)	2882 (5)	3·9 (2)
C(13)	9053 (5)	1034 (4)	3460 (5)	4·3 (2)
C(14)	10367 (5)	1286 (4)	3391 (5)	4·3 (2)
C(15)	10483 (5)	2241 (4)	2745 (6)	5·2 (2)
C(16)	9280 (5)	2978 (4)	2146 (5)	4·5 (2)
C(21)	7891 (6)	4813 (5)	4257 (5)	4·6 (2)

Table 2. *Positional parameters* (×10³), *isotropic thermal parameters and bond lengths for the* H *atoms*

	x	y	z	B_{iso} (Å²)	Bonded to	Bond length (Å)
H(2)	486 (5)	560 (3)	135 (5)	3·3 (1·1)	O(2)	1·03 (4)
H(12)	698 (4)	159 (3)	306 (4)	2·8 (1·0)	C(12)	0·98 (5)
H(13)	895 (5)	36 (4)	397 (5)	5·2 (1·3)	C(13)	0·99 (5)
H(14)	1122 (4)	78 (4)	378 (4)	2·2 (0·9)	C(14)	0·98 (4)
H(15)	1143 (5)	243 (4)	267 (5)	5·0 (1·3)	C(15)	1·00 (6)
H(16)	937 (4)	366 (3)	171 (4)	2·4 (0·9)	C(16)	0·96 (4)
H(31)	502 (4)	423 (3)	406 (4)	2·9 (1·0)	C(3)	0·98 (5)
H(32)	606 (4)	323 (3)	404 (5)	2·8 (1·0)	C(3)	1·01 (4)
H(41)	336 (4)	406 (3)	158 (4)	2·0 (0·9)	C(4)	0·99 (4)
H(42)	354 (4)	281 (3)	229 (4)	2·4 (0·9)	C(4)	1·01 (4)
H(51)	397 (4)	319 (3)	−10 (4)	1·8 (0·9)	C(5)	1·00 (3)
H(52)	480 (4)	220 (3)	96 (4)	1·9 (0·9)	C(5)	1·02 (4)
H(211)	852 (5)	523 (4)	383 (5)	3·3 (1·2)	C(21)	1·02 (5)
H(212)	777 (5)	530 (4)	502 (6)	5·8 (1·5)	C(21)	1·02 (6)
H(213)	848 (5)	410 (4)	477 (5)	5·2 (1·4)	C(21)	1·04 (5)

Discussion. The atom numbering is shown in Fig. 1. Bond distances and angles involving the C, O and P atoms are given in Table 3. Most of the observed values are close to the expected ones but some of them reveal some characteristic differences. The average C—C bond length in the phenyl group is 1·377 Å, which is considerably lower than the standard value of 1·394 Å, possibly because thermal motion was not taken into account. The rigid parts of the molecules are the five-membered rings which form dimeric fragments; the phenyl rings, however, have considerable freedom of movement. This is indicated by the lack of close contact (<3·5 Å) of the ring atoms with those of other molecules and by the noticeable shortening of some bonds in the benzene ring along with small differences in the valency angles. Only two angles have values differing by more than one standard deviation from 120°: C(12)—C(11)—C(16) is 119·0 (3σ) and C(14)—C(15)—C(16) is 121·0° (2σ). Such large deviations (as compared with the remaining values) can, in the first case, be attributed to the known effect of substitution (Domenicano, Vaciago & Coulson, 1975a,b). As for the C(14)—C(15)—C(16) angle, the deviation from the
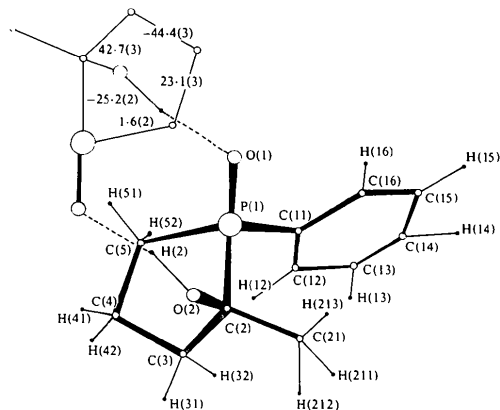
mean value probably results from the error in the determination of the position of C(15). The explanation is substantiated both by the temperature factors, which vary from 1·5 times (for U_{22}) to twice (for U_{33}) as high as the analogous temperature factors for the remaining atoms of the ring, and by the lengths of the C(14)—C(15) and C(15)—C(16) bonds which have the lowest (1·353) and highest (1·395 Å) values in the ring. The atoms of the benzene ring deviate from the least-squares plane by not more than $1·5\sigma_{mean} = 0·006$ Å.

In the solid state, the 2-hydroxy-2-methyl-1-phenylphospholane 1-oxide molecules exist as *RS* dimers. The details of the hydrogen bond are given in Fig. 2 which also shows the packing of the molecules in the unit cell. Except for the hydrogen bond there are no visible distances shorter than the sums of the van der Waals radii.

The five-membered ring is in a nearly ideal C(3) sofa conformation with asymmetry parameters (Duax &

Table 3. *Bond lengths* (Å) *and angles* (°) *for the non-hydrogen atoms*

P(1)—O(1)	1·496 (3)	C(3)—C(4)	1·530 (5)
P(1)—C(2)	1·851 (4)	C(4)—C(5)	1·542 (8)
P(1)—C(5)	1·812 (4)	C(11)—C(12)	1·380 (6)
P(1)—C(11)	1·805 (3)	C(12)—C(13)	1·389 (6)
C(2)—O(2)	1·429 (4)	C(13)—C(14)	1·369 (7)
C(2)—C(3)	1·523 (7)	C(14)—C(15)	1·353 (7)
C(2)—C(21)	1·509 (5)	C(15)—C(16)	1·395 (6)
		C(16)—C(11)	1·378 (7)

O(1)—P(1)—C(2)	115·5 (2)	C(3)—C(2)—C(21)	113·4 (4)
O(1)—P(1)—C(5)	116·3 (2)	C(3)—C(4)—C(5)	108·4 (4)
O(1)—P(1)—C(11)	110·1 (2)	P(1)—C(5)—C(4)	106·3 (3)
C(2)—P(1)—C(5)	96·4 (2)	P(1)—C(11)—C(12)	123·3 (3)
C(2)—P(1)—C(11)	108·4 (2)	P(1)—C(11)—C(16)	117·7 (3)
C(5)—P(1)—C(11)	109·3 (2)	C(11)—C(12)—C(13)	120·4 (4)
P(1)—C(2)—O(2)	108·1 (3)	C(12)—C(13)—C(14)	120·2 (4)
P(1)—C(2)—C(3)	101·9 (3)	C(13)—C(14)—C(15)	119·7 (4)
P(1)—C(2)—C(21)	116·1 (4)	C(14)—C(15)—C(16)	121·0 (5)
O(2)—C(2)—C(3)	110·4 (4)	C(15)—C(16)—C(11)	119·7 (5)
O(2)—C(2)—C(21)	106·9 (3)	C(16)—C(11)—C(12)	119·0 (4)
C(2)—C(3)—C(4)	108·5 (4)		

Fig. 1. View of the molecule normal to the *xz* plane showing the numbering system and torsion angles (°) in the phospholane ring.
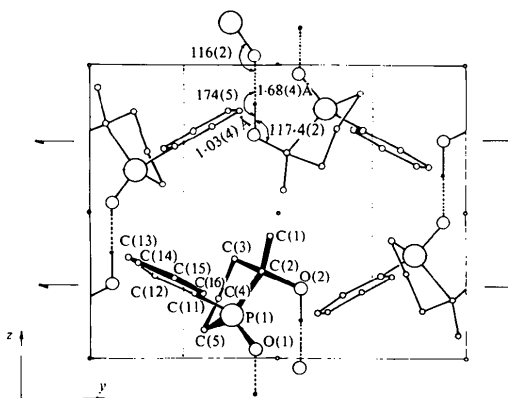

Fig. 2. Packing of the molecules in the unit cell and hydrogen-bonding geometry (Å and deg).

Norton, 1975) $\Delta C_s^3 = 1 \cdot 9$ (3) and $\Delta C_2^5 = 20 \cdot 4$ (3)°. The torsion angles in the ring are given in Fig. 1. The four atoms P(1), C(2), C(4) and C(5) lie in a plane (all σ's $< \sigma_{mean} = 0 \cdot 01$ Å) while C(3) deviates from that plane by $0 \cdot 607$ Å. The angle between the planes of the phenyl and phospholane rings is $86 \cdot 8$ (3)°, whereas in the presence of a C(2)=C(3) double bond conjugation forces the parallelism of the rings (Gałdecki, 1979; Gałdecki & Główka, 1980).

We are indebted to Dr W. Waszkuć for supplying the crystals. This research was supported by project MR.I-9 from the Polish Academy of Sciences.

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Acta Cryst. (1980). B**36**, 2193

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Professor J. M. Cowley, Department of Physics, Arizona State University, USA, and Professor M. M. Woolfson, Department of Physics, University of York, England, have resigned as Co-editors of *Acta Crystallographica*. They have been succeeded by Professor R. Collela, Physics Department, Purdue University, USA, and Dr B. T. M. Willis, Materials Physics Division, AERE Harwell, England. Dr S. Jagner, Department of Inorganic Chemistry, Chalmers University of Technology and University of Göteborg, Sweden, has also been appointed a Co-editor, whilst Dr M. Hospital, Laboratoire de Cristallographie et de Physique Cristalline du CNRS, Talence, France, was appointed a Co-editor earlier this year. The full addresses of all Co-editors of the journal are given on the inside front cover of each issue.

Book Reviews

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Acta Cryst. (1980). B**36**, 2193–2194

Textures of liquid crystals. By D. DEMUS and L. RICHTER. Pp. 228. Weinheim: Verlag Chemie, 1978. Price DM 185.00.

Liquid crystals are the self-ordering phases *par excellence*. Given half a chance, they will usually form complex patterns of loops and whorls, and the bulk phase will be broken down into an intricate array of domains. It is convenient to distinguish between the *texture* of a mesophase at µm–mm level and the *structure* of the mesophase at the immediate intermolecular level. The former is a consequence of the latter (in the sense that the structure of a snowflake is a consequence of the structure of the water molecule) but the interrelation may be far from self-evident and many a newcomer to the subject has spent a fascinating hour or so watching the spontaneous creation and modification of psychedelic patterns – using a polarizing microscope and hot stage – without having the remotest idea of the underlying molecular patterns or of the interplay of physical constraints which give rise to them. This beautifully illustrated book should cater for precisely this situation. The first half of the book is a survey of structure and texture types for the thermotropic phases (nematic and cholesteric phases, and smectics of types *A–G* inclusive). It is well illustrated with a compilation of diagrams mostly selected from the existing literature.

It is the second half of the book, however, which makes it uniquely useful. This is an atlas of optical micrographs of mesophase textures. There are over 200 plates, many in realistic colour. A few examples of lyotropic phases are included but the main emphasis is on the thermotropic, and the authors have made a valiant attempt at a comprehensive survey. We find classic examples of focal conic structures and old friends like MBBA, together with mesophases of controversial or little-understood types, like the smectic *D* and the cholesteric blue phase. This book is therefore very much a 'state of the art' document. Three or four letters have been added to the smectic alphabet since its compilation but