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The Structure of Racemic 7-Benzyl-4-*tert*-butyl-9-hydroxy-8-phenyl-7-phospha-*cis*-bicyclo[4.3.0]non-8-ene *anti*-7-Oxide*

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Abstract. $C_{25}H_{31}O_2P$, $M_r = 394{\cdot}51$, monoclinic, $P2_1/n$, $Z = 4$, $a = 11{\cdot}46\,(1)$, $b = 8{\cdot}62\,(1)$, $c = 22{\cdot}09\,(2)$ Å, $\beta = 93{\cdot}80\,(1)°$, $V = 2177{\cdot}4$ Å^3, $D_m = 1{\cdot}194$ (by flotation), $D_x = 1{\cdot}203$ Mg m^{-3}, $F(000) = 848$. The structure was solved by *MULTAN* and refined to a final R of 0·046 ($R_w = 0{\cdot}050$) for 2514 independent reflections. Both rings are in the sofa conformation with asymmetry parameters $\Delta C_s^{\min} = 1{\cdot}6$, $\Delta C_2^{\min} = 16{\cdot}8°$ for the phospholene and $\Delta C_s^{\min} = 1{\cdot}1$, $\Delta C_2^{\min} = 7{\cdot}7°$ for the fused cyclohexane rings. The rings have a *cis* junction and the phosphoryl O atom is *anti* to the H(8) atom.

Introduction. This study is a continuation of our X-ray investigations of the structures and conformations of phosphaindole derivatives (Gałdecki, 1979), which are intermediates in the syntheses of steroid analogues containing a P atom (Bodalski & Pietrusiewicz, 1977). From this point of view the 7-phosphabicyclo[4.3.0]-non-8-ene system is very interesting because of the different conformations and configurations possible. Synthesis of the title compound leads to the racemate, although a new chiral center at the P atom is formed (Bodalski & Pietrusiewicz, 1977). On the basis of NMR data a *cis* conformation was proposed, with the O atom of the phosphoryl group turned towards the fused cyclohexane ring. The significance of the problem induced us to determine the structure by the X-ray method. Besides, phospholene derivatives have not been extensively examined, especially when the phospholene unit is fused to other rings. Only five other structures containing a P atom in similar five-membered rings have been reported: the 1-oxides of 1-hydroxyphospholane (Alver & Kjøge, 1969), 1-benzyl-3-hydroxy-4,5-dimethyl-2-phenylphosphol-2-ene (Washecheck, Helm, Purdum & Berlin, 1974), 1-benzylphosphole (Coggon, Engel, McPhail & Quin, 1970), and 1-hydroxydibenzo-1*H*-phosphole (Boer & Bright, 1974), and 7-benzyl-9-methoxy-8-phenyl-7-phosphabicyclo[4.3.0]non-8-ene 7-oxide (I) (Gałdecki, 1979). We now report the crystal structure analysis of 7-benzyl-4-*tert*-butyl-9-hydroxy-8-phenyl-7-phosphabicyclo[4.3.0]non-8-ene 7-oxide (II).

Intensities were collected on a CAD-4 diffractometer (Cu $K\alpha$ radiation) from a spherical crystal of diameter ~0·3 mm. The 2514 independent reflections were reduced to 2369 by the criterion $F > 3\sigma(F)$. Accurate cell dimensions were derived from 25 high-order reflections. The structure was solved by direct methods (*MULTAN*; Germain, Main & Woolfson, 1971). The E map based on 332 $E \geq 1{\cdot}50$ gave the positions of all the atoms but one, which was located on the Fourier map ($R = 0{\cdot}27$). Full-matrix and block-diagonal least-squares refinement converged at $R = 0{\cdot}046$, $R_w = 0{\cdot}050$. The weights were $w^{-1} = \sigma^2(F)$.

Neutral-atom scattering factors for P, O and C atoms were taken from Doyle & Turner (1968) and for H from *International Tables for X-ray Crystallography* (1962). The calculations were processed using the XRAY 70 system (Stewart, Kundell & Baldwin, 1970) on a RIAD 22 computer.

Discussion. Positional and isotropic thermal parameters are given in Tables 1 and 2.† Bond lengths and angles are in Tables 3 and 4 respectively. A view of the molecule and the numbering system are shown in Fig. 1. The molecules are packed in the crystal nearly parallel to the y axis (Fig. 2); they are connected by hydrogen bonds, $\geq$P=O(1)···H–O(2)–C(3), with O···O = 2·61 Å.

Fig. 3 shows the torsion angles and asymmetry parameters (Duax & Norton, 1975) for (I) and (II). The conformations of the compounds are similar except that the five-membered ring adopts a C(8) sofa conformation in (II) and a conformation intermediate between C(8) sofa and C(2) half-chair in (I). The four atoms P(1), C(2), C(3) and C(9) lie nearly in a plane ($\sigma_{\text{mean}} = 0{\cdot}0097$ Å) while C(8) deviates from that plane

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* Conformational Studies of 7-Phosphabicyclo[4.3.0]non-8-ene 7-Oxides. II.

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35293 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Positional parameters* (×10⁴) *and isotropic thermal parameters for the non-hydrogen atoms with their e.s.d.'s in parentheses*

	x	y	z	B_{iso} (Å^2)
P(1)	8893 (1)	6630 (1)	3368 (1)	2·8 (1)
O(1)	9326 (2)	8258 (2)	3293 (1)	3·7 (1)
O(2)	5995 (2)	5461 (2)	2511 (1)	3·8 (1)
C(2)	7354 (2)	6353 (3)	3284 (1)	2·5 (1)
C(3)	7092 (2)	5701 (3)	2734 (1)	2·9 (1)
C(4)	8250 (3)	6578 (3)	1860 (1)	3·6 (2)
C(5)	9417 (3)	6390 (4)	1562 (1)	3·9 (2)
C(6)	10467 (3)	6522 (3)	2029 (1)	3·3 (1)
C(7)	10373 (3)	5257 (3)	2518 (1)	3·9 (2)
C(8)	9189 (2)	5202 (3)	2795 (1)	3·0 (1)
C(9)	8096 (2)	5322 (3)	2346 (1)	3·3 (1)
C(10)	9517 (3)	5940 (4)	4096 (1)	4·0 (2)
C(11)	9200 (2)	4331 (4)	4294 (1)	3·4 (2)
C(12)	9834 (3)	3054 (4)	4123 (2)	4·8 (2)
C(13)	9579 (3)	1576 (4)	4330 (2)	5·4 (2)
C(14)	8701 (3)	1362 (4)	4711 (2)	5·5 (2)
C(15)	8050 (3)	2603 (4)	4879 (2)	5·3 (2)
C(16)	8290 (3)	4088 (4)	4668 (1)	4·3 (2)
C(17)	11680 (3)	6481 (4)	1740 (2)	4·8 (2)
C(18)	12679 (3)	6494 (4)	2238 (2)	5·4 (2)
C(19)	11806 (3)	5032 (4)	1336 (2)	5·5 (2)
C(20)	11786 (3)	7946 (4)	1348 (2)	5·3 (2)
C(21)	6563 (3)	6809 (3)	3745 (1)	3·2 (1)
C(22)	6899 (3)	7962 (3)	4166 (1)	4·0 (2)
C(23)	6212 (3)	8323 (4)	4645 (1)	4·8 (2)
C(24)	5193 (3)	7533 (4)	4714 (2)	4·9 (2)
C(25)	4833 (3)	6411 (4)	4289 (2)	5·1 (2)
C(26)	5499 (3)	6053 (4)	3814 (1)	4·3 (2)

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

	x	y	z	B_{iso} (Å^2)	Bonded to	Bond length (Å)
H(1)	599 (3)	471 (4)	227 (1)	6·0 (9)	O(2) O(1)	0·84 (3) 1·78 (3)
H(41)	757 (2)	654 (3)	152 (1)	2·4 (6)	C(4)	1·05 (2)
H(42)	819 (2)	777 (3)	208 (1)	2·4 (6)	C(4)	1·13 (2)
H(51)	940 (3)	732 (4)	116 (1)	4·3 (8)	C(5)	1·19 (3)
H(52)	941 (2)	538 (3)	134 (1)	3·2 (7)	C(5)	1·00 (2)
H(6)	1043 (2)	769 (3)	225 (1)	1·1 (6)	C(6)	1·13 (2)
H(71)	1047 (2)	437 (3)	236 (1)	1·4 (6)	C(7)	0·85 (2)
H(72)	1115 (3)	533 (4)	293 (1)	5·5 (9)	C(7)	1·23 (3)
H(8)	915 (2)	415 (3)	303 (1)	1·3 (6)	C(8)	1·04 (2)
H(9)	978 (2)	422 (3)	218 (1)	2·1 (6)	C(9)	1·03 (3)
H(101)	1043 (3)	601 (3)	401 (1)	4·0 (8)	C(10)	1·07 (3)
H(102)	932 (2)	677 (3)	439 (1)	2·8 (7)	C(10)	1·00 (3)
H(12)	952 (2)	673 (3)	622 (1)	2·8 (7)	C(12)	1·11 (3)
H(13)	1005 (3)	71 (4)	426 (2)	7·8 (11)	C(13)	0·95 (4)
H(14)	857 (3)	24 (4)	487 (2)	5·8 (9)	C(14)	1·05 (4)
H(15)	743 (4)	225 (4)	516 (2)	7·7 (11)	C(15)	1·02 (4)
H(16)	779 (2)	500 (3)	478 (1)	3·5 (7)	C(16)	1·02 (2)
H(181)	1339 (3)	668 (3)	205 (2)	4·5 (9)	C(18)	0·96 (3)
H(182)	1255 (2)	739 (3)	253 (1)	3·2 (7)	C(18)	1·02 (2)
H(183)	1274 (4)	545 (5)	259 (2)	10·3 (14)	C(18)	1·19 (5)
H(191)	1175 (3)	389 (4)	153 (2)	6·9 (10)	C(19)	1·08 (4)
H(192)	1255 (3)	501 (4)	115 (2)	6·9 (10)	C(19)	0·97 (4)
H(193)	1116 (4)	487 (4)	88 (2)	8·4 (12)	C(19)	1·21 (4)
H(201)	1114 (3)	809 (3)	103 (1)	4·0 (8)	C(20)	0·99 (3)
H(202)	1172 (3)	918 (5)	161 (2)	8·6 (12)	C(20)	1·22 (5)
H(203)	1248 (3)	798 (3)	117 (1)	3·8 (7)	C(20)	0·92 (3)
H(22)	766 (2)	850 (3)	416 (1)	2·1 (6)	C(22)	0·99 (2)
H(23)	649 (2)	923 (3)	496 (1)	3·4 (7)	C(23)	1·08 (2)
H(24)	469 (3)	794 (3)	506 (1)	4·1 (8)	C(24)	1·05 (3)
H(25)	414 (2)	591 (3)	430 (1)	3·0 (7)	C(25)	0·91 (2)
H(26)	519 (2)	524 (3)	349 (1)	2·3 (6)	C(26)	1·05 (2)

Table 3. *Bond lengths* (Å)

P(1)–O(1)	1·501 (3)	C(11)–C(12)	1·385 (5)
P(1)–C(2)	1·778 (3)	C(12)–C(13)	1·391 (5)
P(1)–C(8)	1·814 (3)	C(13)–C(14)	1·366 (5)
P(1)–C(10)	1·816 (3)	C(14)–C(15)	1·369 (5)
O(2)–C(3)	1·336 (3)	C(15)–C(16)	1·395 (5)
C(2)–C(3)	1·354 (4)	C(16)–C(11)	1·389 (4)
C(2)–C(21)	1·463 (4)	C(17)–C(6)	1·568 (5)
C(3)–C(9)	1·515 (4)	C(18)–C(17)	1·534 (5)
C(4)–C(5)	1·537 (4)	C(19)–C(17)	1·548 (5)
C(5)–C(6)	1·537 (4)	C(20)–C(17)	1·541 (5)
C(6)–C(7)	1·544 (4)	C(21)–C(22)	1·398 (4)
C(7)–C(8)	1·526 (4)	C(22)–C(23)	1·394 (5)
C(8)–C(9)	1·548 (4)	C(23)–C(24)	1·370 (5)
C(9)–C(4)	1·543 (4)	C(24)–C(25)	1·391 (5)
C(10)–C(11)	1·506 (5)	C(25)–C(26)	1·374 (5)
		C(26)–C(21)	1·399 (4)

Table 4. *Bond angles* (°)

O(1)–P(1)–C(2)	116·5 (1)	C(6)–C(7)–C(8)	114·1 (2)
O(1)–P(1)–C(8)	118·6 (1)	C(6)–C(17)–C(18)	110·3 (2)
O(1)–P(1)–C(10)	106·9 (1)	C(6)–C(17)–C(19)	111·9 (2)
C(2)–P(1)–C(8)	93·7 (1)	C(6)–C(17)–C(20)	108·4 (2)
C(2)–P(1)–C(10)	112·3 (1)	C(7)–C(8)–C(9)	116·4 (2)
C(8)–P(1)–C(10)	108·3 (2)	C(7)–C(6)–C(17)	112·0 (2)
P(1)–C(2)–C(3)	108·1 (2)	C(10)–C(11)–C(12)	120·8 (3)
P(1)–C(2)–C(21)	123·2 (2)	C(10)–C(11)–C(16)	121·1 (3)
P(1)–C(8)–C(7)	118·1 (2)	C(11)–C(12)–C(13)	120·8 (3)
P(1)–C(8)–C(9)	102·8 (2)	C(11)–C(16)–C(15)	120·6 (3)
P(1)–C(10)–C(11)	118·1 (2)	C(12)–C(11)–C(16)	118·1 (3)
O(2)–C(3)–C(2)	122·9 (3)	C(12)–C(13)–C(14)	120·4 (3)
O(2)–C(3)–C(9)	119·4 (2)	C(13)–C(14)–C(15)	119·9 (3)
C(2)–C(3)–C(9)	117·7 (2)	C(14)–C(15)–C(16)	120·2 (3)
C(2)–C(21)–C(22)	119·9 (3)	C(18)–C(17)–C(19)	109·0 (3)
C(2)–C(21)–C(26)	122·3 (3)	C(18)–C(17)–C(20)	108·4 (3)
C(3)–C(2)–C(21)	128·8 (3)	C(19)–C(17)–C(20)	108·9 (3)
C(3)–C(9)–C(4)	111·6 (2)	C(21)–C(22)–C(23)	121·2 (3)
C(3)–C(9)–C(8)	105·4 (2)	C(21)–C(26)–C(25)	120·7 (3)
C(4)–C(9)–C(8)	111·6 (2)	C(22)–C(21)–C(26)	117·6 (3)
C(4)–C(5)–C(6)	111·7 (2)	C(22)–C(23)–C(24)	120·2 (3)
C(5)–C(6)–C(7)	109·2 (2)	C(23)–C(24)–C(25)	119·1 (3)
C(5)–C(4)–C(9)	111·5 (2)	C(24)–C(25)–C(26)	121·2 (3)
C(5)–C(6)–C(17)	113·6 (2)		

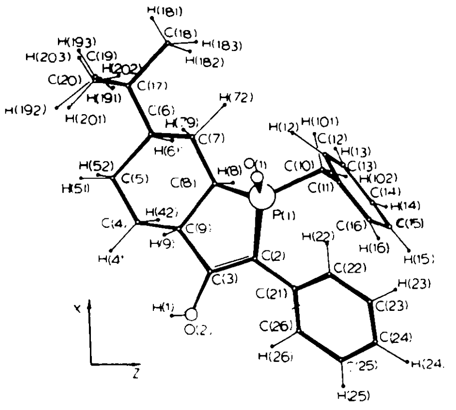

Fig. 1. The molecule viewed parallel to the [010] direction, showing the numbering system.

by 0·60 Å. The rings are *cis*-fused and H(8) is *anti* to the phosphoryl group.

The bond lengths and valency angles in (II) are also close to the corresponding values in (I). Considerable differences can be seen in the angles of the phosphorus tetrahedron, except for that inside the phospholene ring. The values are: 112·7 (I) and 106·9 (II) for O(1)–P(1)–C(10), 107·3 (I) and 112·3 (II) for C(2)–P(1)–C(10), and 105·4 (I) and 108·3° (II) for C(8)–P(1)–C(10). The observed differences are likely to result from the position of the C(10) atom.

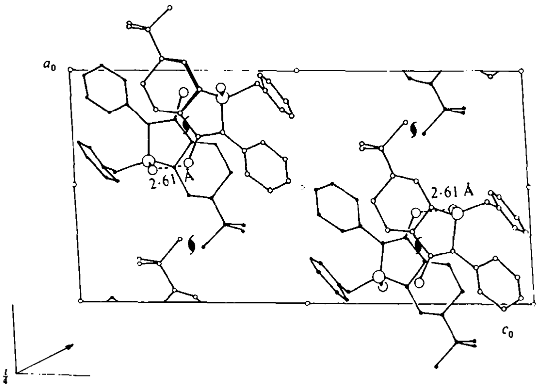

Fig. 2. Packing of the molecules in the unit cell.

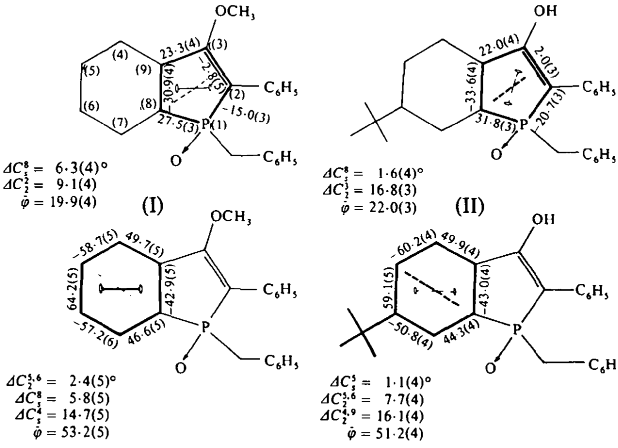

Fig. 3. Conformation of the 7-phosphabicyclo[4.3.0]non-8-ene system, showing the torsion angles (°).

As usual, the P–C(sp^3) lengths (1·814 and 1·816 Å) are longer than the P–C(sp^2) length (1·778 Å). The C(2)=C(3) bond appears to be slightly longer than a pure alkene bond (~1·335 Å). This is correlated with the torsion angle of 2·0 (3)° for P(1)–C(2)–C(3)–C(9). The lengthening probably results from conjugation of the π electrons of the double bond with a lone electron pair of O(2) and with the π electron of the phenyl substituent at C(2). Such a conjugation is indicated by the clear shortening of C(3)–O(2) from 1·43 to 1·375 (I) and 1·336 Å (II) and C(2)–C(21) from 1·53 to 1·476 (I) and 1·463 Å (II).

Generally speaking, the bond lengths and valency angles in the present structure (II) are closer to the mean literature values than those in (I).

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