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Structure and Absolute Configuration of Enantiomeric (+)-(*S*)-3-[Benzyl(phenyl)phosphinoyl]-2-butenoic Acid: Determination of the Structure by its Similarity to that of the Racemate

By M. L. Główka

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

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Abstract. $C_{17}H_{17}O_3P$, $M_r = 300{\cdot}3$, monoclinic, space group $P2_1$, $Z = 4$, $a = 9{\cdot}147$ (3), $b = 10{\cdot}294$ (3), $c = 16{\cdot}911$ (4) Å, $\beta = 98{\cdot}08$ (4)°, $V = 1576{\cdot}5$ Å^3, $D_o = 1{\cdot}264$ (by flotation), $D_x = 1{\cdot}265$ Mg m^{-3}, $F(000) = 632$. The structure was determined by its similarity to that of the racemate [Główka (1978). *Acta Cryst.* B**34**, 3089–3091] and refined by least squares to a final $R = 0{\cdot}074$ and $R_w = 0{\cdot}062$ for a total of 2149 observed reflections. The two independent molecules have similar antiplanar C=C–C=O conformations with a nearly flat O=P–C(CH$_3$)=C(H)–C(OH)=O system. The molecules are linked by means of hydrogen bonds $\geqslant$P=O···OH– to form two independent chains for the two types of molecules along 2_1 axes.

Introduction. Enantiomeric 3-[benzyl(phenyl)phosphinoyl]-2-propenoic acid was used by Bodalski & Koszuk (1982) in the stereospecific synthesis of 3-hydroxy-1,2-diphenyl-1-phosphabicyclo[4.3.0]non-2-ene 1-oxides. These phosphaindole-like derivatives are the intermediates in the stereospecific synthesis of steroid analogues containing a P atom and the knowledge of the absolute configuration of the acid was desired. Though the compound examined, 3-[benzyl(phenyl)phosphinoyl]-2-butenoic acid, differs from the acid used in the reaction mentioned above in having a methyl group at the double bond, the absolute configuration of both molecules should be the same. We are also interested in the stereochemistry and hydrogen bonding in crystals of phosphine oxide derivatives containing a carboxylic group in the molecule (Gałdecki & Główka, 1977*a*,*b*, 1978). Leiserowitz (1976, and references therein) discussed exhaustively the hydrogen bonding and geometry of α,β-unsaturated carboxylic acids, but in the presence of the phosphoryl group in this molecule, $\geqslant$P=O···HO– hydrogen bonds are formed instead of $>$C=O···HO–.

Prismatic crystals of the compound were obtained by slow cooling of the saturated solution in hot aqueous acetone. 2359 intensities were collected from an unshaped crystal by means of a Syntex $P2_1$ four-circle diffractometer and graphite-monochromated Cu $K\alpha$ radiation; 2149 with $F_o > 2\sigma F_o$ were considered as observed and used in the refinement. Measurements were carried out in the θ–2θ mode up to $2\theta = 115°$.

Several attempts to solve the structure by means of Patterson and direct methods failed and, in retrospect, this seems to be due to a pseudo-*n*-glide relation between the independent molecules in the [010] projection of the structure. It was noted that there was a close correspondence in both positions and intensities between the (*h*0*l*) reciprocal lattices of the present compound and the racemate (Główka, 1978) provided the present cell was transformed by $\bar{1}00/0\bar{1}0/101$ as shown in Fig. 2. This suggested that the enantiomeric molecules related by the *c* glide in the racemate $P2_1/c$ are now identical in chirality but conform to a very similar [010] projection.

Accordingly, the flat fragment of one molecule found in the racemic crystal was initially placed in the unit cell of the enantiomer with due allowance for the cell transformation and gave $R = 0{\cdot}42$. The remaining atoms were located from subsequent Fourier maps. The structure was then refined by full-matrix, block-diagonal and free-blocking least squares. After six cycles of full-matrix isotropic refinement ($R = 0{\cdot}128$, $R_w = 0{\cdot}137$) and a further five cycles of block-diagonal refinement with anisotropic temperature factors ($R = 0{\cdot}085$, $R_w = 0{\cdot}074$), the coordinates of all H atoms except those in the hydroxyl groups were calculated geometrically. Next the refinement of heavy-atom parameters was repeated because of weak convergence during the block-diagonal least-squares procedure. Each of the two independent molecules in turn was refined by full-matrix least squares for two anisotropic cycles (four cycles in all) while the other was fixed because there were too many variables. The H atoms were given isotropic temperature factors equal to those of their parent heavy atoms and were not refined. The final agreement factors R and R_w including H atoms were 0·074 and 0·062 respectively and all structural parameters listed in the paper refer to these values. The weighting scheme used was $w^{-2} = \sigma(F)$. Neutral scattering factors for P, O and C atoms were taken from Doyle & Turner (1968) and for H from

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International Tables for X-ray Crystallography (1962). The calculations were processed using the XRAY 70 system (Stewart, Kundell & Baldwin, 1970) and a Riad 32 computer.*

Discussion. The heavy-atom parameters are listed in Table 1. Fig. 1 shows the molecules viewed along **a** with the atom-numbering scheme. A considerable part of both the independent molecules is almost flat as a result of the conjugated system of double bonds. The conformations of the molecules are generally similar and the flat fragments resemble the conformation found in the racemic crystal (Główka, 1978). The molecules of types I and II form independent chains by means of hydrogen bonding, $\geq$P=O···HO–. O(1)···O(2) distances of 2·627 (9) and 2·606 (9) Å for chains of molecules I and II respectively are in good agreement with 2·587 Å observed in the structure of the racemate. The chains formed from flat fragments of molecules are arranged into ribbons running along the 2_1 screws and lying roughly parallel to [100]. The phenyl and benzyl substituents fill the space between the ribbons (Fig. 2).

The molecules have the antiplanar C=C–C=O conformation contrary to the synplanar one hitherto usually found in α,β-unsaturated monocarboxylic acids (Leiserowitz, 1976). A similar antiplanar arrangement was observed in *trans*-cinnamic acid (Ladell, McDonald & Schmidt, 1956) and in fumaric acid (Brown, 1966; Bednowitz & Post, 1966).

The differences in bond lengths and angles between the two molecules are distinct but usually not greater than 3σ. For example, the P–C(1) bond length is 1·812 (10) in (I) and 1·802 (10) Å in (II). The most

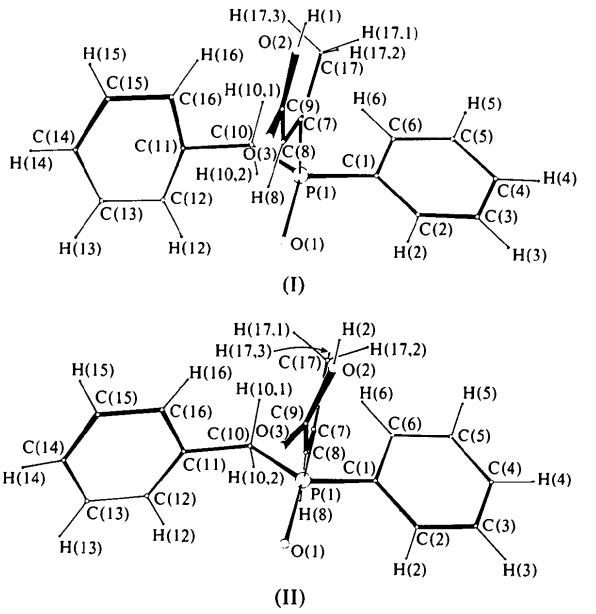

Fig. 1. The crystallographically independent molecules (I at the top, II at the bottom) viewed in the [100] direction, and numbering of atoms. The configuration shown is that for the (+)*S* enantiomer.

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36023 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Non-*H*-atom parameters (positional* $\times 10^4$*) with e.s.d.'s in parentheses*

$$B_{iso} = \tfrac{8}{3}\pi^2 \sum_i \sum_j (U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j).$$

	Molecule I				Molecule II			
	x	*y*	*z*	B_{iso} (Å^2)	*x*	*y*	*z*	B_{iso} (Å^2)
P	1351 (2)	2500	−55 (1)	3·30 (7)	6373 (2)	115 (2)	5065 (1)	3·40 (8)
O(1)	1810 (6)	3866 (6)	−254 (4)	4·4 (2)	6764 (6)	1481 (6)	4852 (4)	4·6 (2)
O(2)	5592 (8)	−57 (8)	−163 (5)	7·0 (3)	10883 (7)	−2247 (7)	5402 (4)	5·4 (2)
O(3)	6542 (9)	1734 (11)	−496 (9)	13·4 (6)	11622 (8)	−556 (8)	4758 (6)	8·5 (4)
C(1)	882 (9)	2424 (9)	950 (5)	4·3 (3)	5721 (8)	59 (9)	6021 (5)	4·1 (3)
C(2)	1713 (11)	3205 (11)	1524 (6)	5·4 (4)	6315 (11)	1012 (11)	6588 (6)	5·8 (4)
C(3)	1340 (12)	3195 (13)	2296 (7)	6·2 (5)	5816 (11)	954 (13)	7344 (7)	6·8 (5)
C(4)	266 (12)	2400 (13)	2511 (6)	6·5 (4)	4841 (12)	−2 (15)	7531 (7)	7·6 (5)
C(5)	−535 (14)	1628 (14)	1943 (8)	8·0 (5)	4318 (12)	−921 (14)	6969 (7)	7·2 (5)
C(6)	−229 (11)	1641 (12)	1150 (6)	5·7 (4)	4738 (10)	−901 (11)	6204 (6)	5·2 (4)
C(7)	2842 (9)	1324 (9)	−78 (5)	4·0 (5)	7946 (9)	−983 (9)	5169 (5)	3·6 (3)
C(8)	4084 (8)	1824 (10)	−301 (5)	4·3 (3)	9230 (8)	−423 (9)	5083 (6)	3·9 (3)
C(9)	5511 (11)	1124 (12)	−308 (6)	5·5 (4)	10692 (8)	−1082 (10)	5072 (6)	4·3 (3)
C(10)	−222 (9)	1924 (10)	−715 (5)	4·4 (3)	4930 (9)	−564 (10)	4348 (6)	4·4 (3)
C(11)	−12 (9)	2029 (10)	−1590 (6)	4·6 (4)	5213 (10)	−402 (10)	3497 (6)	4·5 (3)
C(12)	−579 (12)	3134 (13)	−2028 (6)	6·3 (4)	4450 (17)	594 (15)	3030 (7)	8·8 (6)
C(13)	−401 (14)	3207 (14)	−2847 (8)	7·7 (5)	4799 (19)	749 (16)	2242 (8)	10·3 (7)
C(14)	269 (12)	2177 (14)	−3203 (7)	7·2 (5)	5778 (15)	−85 (16)	1919 (7)	8·5 (6)
C(15)	773 (12)	1107 (14)	−2790 (6)	6·5 (4)	6363 (12)	−1083 (14)	2352 (7)	7·0 (5)
C(16)	650 (11)	1013 (11)	−1965 (7)	5·7 (4)	6201 (11)	−1217 (13)	3177 (6)	6·0 (4)
C(17)	2504 (13)	−80 (10)	158 (7)	6·5 (4)	7660 (10)	−2409 (9)	5324 (6)	4·9 (3)

Table 2. *Bond lengths* (Å) *observed in the enantiomeric crystal*

	Molecule I	Molecule II
P–O(1)	1·519 (6)	1·507 (7)
P–C(1)	1·812 (10)	1·802 (10)
P–C(7)	1·829 (9)	1·819 (9)
P–C(10)	1·794 (9)	1·802 (9)
C(1)–C(2)	1·399 (13)	1·425 (14)
C(2)–C(3)	1·394 (15)	1·418 (16)
C(3)–C(4)	1·367 (17)	1·393 (19)
C(4)–C(5)	1·375 (18)	1·379 (19)
C(5)–C(6)	1·407 (18)	1·400 (17)
C(6)–C(1)	1·377 (15)	1·399 (14)
C(7)–C(8)	1·349 (12)	1·334 (12)
C(7)–C(17)	1·542 (15)	1·520 (13)
C(8)–C(9)	1·492 (14)	1·502 (12)
C(9)–O(2)	1·240 (15)	1·324 (12)
C(9)–O(3)	1·213 (15)	1·195 (13)
C(10)–C(11)	1·521 (14)	1·508 (14)
C(11)–C(12)	1·416 (16)	1·416 (17)
C(12)–C(13)	1·420 (17)	1·422 (20)
C(13)–C(14)	1·402 (20)	1·406 (23)
C(14)–C(15)	1·350 (19)	1·330 (20)
C(15)–C(16)	1·418 (16)	1·429 (16)
C(16)–C(11)	1·404 (15)	1·397 (15)

Table 3. *Valence angles* (°)

	Molecule I	Molecule II
O(1)–P–C(1)	111·0 (4)	111·4 (4)
O(1)–P–C(7)	112·2 (4)	113·1 (4)
O(1)–P–C(10)	113·0 (4)	112·2 (4)
C(1)–P–C(7)	105·5 (4)	104·5 (4)
C(1)–P–C(10)	107·2 (4)	106·7 (4)
C(7)–P–C(10)	107·6 (4)	108·6 (4)
P–C(1)–C(2)	116·7 (7)	116·0 (7)
P–C(1)–C(6)	122·4 (7)	121·7 (7)
C(2)–C(1)–C(6)	120·9 (9)	122·2 (9)
C(1)–C(2)–C(3)	117·7 (10)	115·9 (10)
C(2)–C(3)–C(4)	122·2 (11)	122·1 (11)
C(3)–C(4)–C(5)	119·5 (11)	119·9 (11)
C(4)–C(5)–C(6)	120·2 (12)	120·9 (12)
C(5)–C(6)–C(1)	119·4 (10)	118·9 (10)
P–C(7)–C(8)	114·4 (7)	114·7 (7)
P–C(7)–C(17)	116·0 (7)	117·6 (6)
C(8)–C(7)–C(17)	129·6 (9)	127·7 (8)
C(7)–C(8)–C(9)	126·1 (9)	127·2 (8)
O(2)–C(9)–O(3)	122·1 (10)	122·6 (8)
O(2)–C(9)–C(8)	120·1 (9)	118·0 (7)
O(3)–C(9)–C(8)	117·7 (11)	119·5 (9)
P–C(10)–C(11)	112·4 (6)	113·1 (6)
C(10)–C(11)–C(12)	118·6 (9)	118·4 (9)
C(10)–C(11)–C(16)	120·5 (9)	120·7 (9)
C(12)–C(11)–C(16)	120·8 (10)	120·9 (10)
C(11)–C(12)–C(13)	118·0 (11)	116·5 (13)
C(12)–C(13)–C(14)	119·7 (12)	122·3 (14)
C(13)–C(14)–C(15)	122·2 (12)	119·1 (12)
C(14)–C(15)–C(16)	119·7 (12)	121·6 (12)
C(15)–C(16)–C(11)	119·5 (10)	118·8 (10)

improbable value is 1·24 (2) Å for O(2)–C(9) in (I). C–C bond lengths in the benzene rings differ considerably from the 'standard' value of 1·395 Å, especially in the benzyl substituent [1·35 (2) for C(14)–C(15) in (I) and 1·33 (2) Å in (II)] (Table 2). Similar differences may be found in valence angles, for example, 116 (1)° for both C(1)–C(2)–C(3) and C(11)–C(12)–C(13) in (II). Repulsive interactions between the methyl at C(7) and carboxyl –C(8) groups cause an increase in the C(17)–C(7)=C(8) and C(7)=C(8)–C(9) angles to about 126–130° and decrease of the C(17)–C(7)–P and P–C(7)=C(8) valency angles to 114–117° (Table 3). As usual in a compound of the type R_3P=O, the P coordinating tetrahedron is deformed by increasing the O=P–C valence angles to a mean value of 112° with a simultaneous decrease of the C–P–C angles to about 107°.

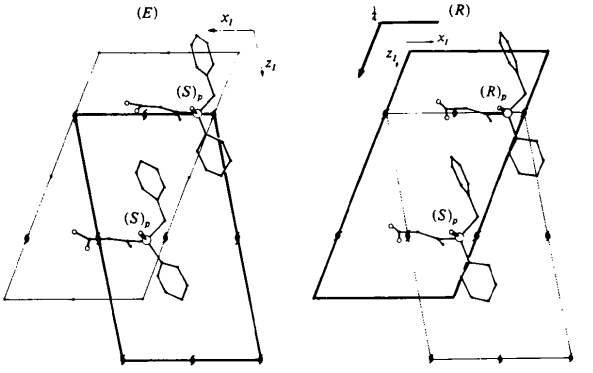

Fig. 2. Packing of the molecules in the unit cell of the enantiomeric crystal (*E*) as compared with that in the racemic crystal (*R*).

The Bijvoet pairs were not available. The absolute-configuration determination was attempted by refinement of the crystal-structure parameters in three cycles of least squares, allowing for the anomalous dispersion of the P and O atoms (Cromer & Liberman, 1970). The final R (R_w) factors were 0·0728 (0·0606) for molecules of the proposed (+)*S* (Fig. 1) configuration and 0·0750 (0·0631) for the opposite configuration. The significance test on the R factor ratio (Hamilton, 1965) shows the probability of an error in determination of the absolute configuration to be much less than 0·5%. $\mathcal{R}_{1,1770,0\cdot005} = 1\cdot003$; $R_1/R_2 = 1\cdot030$, $R_{w1}/R_{w2} = 1\cdot041$.

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Structure of 1-[Benzyl(phenyl)phosphinoyl]-1-phenylethanol

BY M. L. GŁÓWKA AND Z. GAŁDECKI

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

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Abstract. $C_{21}H_{21}O_2P$, $M_r = 336{\cdot}37$, monoclinic, $P2_1/c$, $Z = 4$, $a = 8{\cdot}765\,(2)$, $b = 20{\cdot}224\,(4)$, $c = 10{\cdot}182\,(2)$ Å, $\beta = 97{\cdot}21\,(2)°$, $V = 1790{\cdot}6$ Å^3, $D_o = 1{\cdot}23$ (flotation), $D_c = 1{\cdot}247$ Mg m^{-3}, $F(000) = 712$. The structure was solved with *MULTAN* and refined by least squares to a final R of 0·047 ($R_w = 0{\cdot}036$) for all 1658 intensities collected on a diffractometer with Cu radiation. The molecules form chains by means of hydrogen bonds with an O···O distance of 2·693 Å. The chains run along glide planes. The hydroxyl group is in an antiperiplanar position with respect to the phosphinoyl oxygen.

Introduction. The present investigation is part of our study on the structures, conformations and hydrogen bonding in phosphine oxide derivatives containing a hydroxyl group (Gałdecki & Główka, 1980*a*,*b*,*c*, 1981). Colourless crystals of the compound were kindly furnished by Dr W. Waszkuć from the Institute of Organic Chemistry, Technical University of Łódź. Intensities from a spherical crystal (about 0·3 mm in diameter) were recorded on a CAD-4 diffractometer with graphite-monochromated Cu $K\alpha$ radiation. All the 1658 independent intensities were used in the refinement. Absorption was neglected. The calculations were performed by means of the XRAY 76 system (Stewart, 1976) on a Riad 22 computer, and *MULTAN* (Germain, Main & Woolfson, 1971) on an Odra 1305 machine. The weighting scheme applied was $w^{-2} = \sigma(F_o)$.

The structure was solved with *MULTAN* based on 200 $E > 1{\cdot}553$. Three cycles of refinement by full-matrix least squares with isotropic temperature factors followed by two anisotropic cycles (block-diagonal) enabled us to locate all the H atoms on a difference Fourier map. The H atoms were refined in two cycles by full-matrix least squares, and finally three cycles of block-diagonal refinement of the parameters of all the atoms (H isotropic, remaining atoms anisotropic) were carried out. The final R and R_w

Table 1. *Positional parameters* ($\times 10^4$) *and temperature factors* (Å^2 $\times 10^3$) *for the non-hydrogen atoms*

$$U_{eq} = \tfrac{1}{3}\sum_i\sum_j U_{ij}\, a_i^*\, a_j^*\, \mathbf{a}_i\cdot\mathbf{a}_j.$$

	x	y	z	U_{eq}
P	10904 (3)	6873 (1)	2313 (3)	36 (2)
O(1)	10849 (7)	7023 (3)	862 (6)	40 (4)
O(2)	9377 (7)	7003 (3)	4410 (7)	44 (4)
C(1)	7795 (10)	6677 (4)	2414 (10)	34 (6)
C(2)	7353 (11)	6674 (6)	1059 (11)	51 (8)
C(3)	6127 (12)	6281 (6)	517 (13)	69 (9)
C(4)	5353 (13)	5898 (6)	1333 (13)	69 (9)
C(5)	5746 (12)	5901 (5)	2671 (13)	64 (8)
C(6)	6994 (11)	6290 (5)	3238 (12)	51 (7)
C(7)	9113 (10)	7117 (4)	3028 (10)	32 (6)
C(8)	8748 (11)	7848 (5)	2710 (11)	47 (7)
C(10)	12544 (10)	7262 (5)	3333 (11)	42 (6)
C(11)	13108 (10)	7889 (5)	2763 (10)	39 (6)
C(12)	12659 (11)	8503 (5)	3182 (12)	54 (7)
C(13)	13223 (13)	9080 (5)	2676 (14)	74 (9)
C(14)	14246 (13)	9038 (6)	1756 (14)	77 (9)
C(15)	14708 (12)	8432 (7)	1337 (13)	70 (9)
C(16)	14135 (11)	7855 (6)	1836 (12)	55 (7)
C(21)	11134 (10)	5995 (4)	2646 (10)	39 (6)
C(22)	11087 (13)	5576 (5)	1568 (13)	61 (8)
C(23)	11317 (17)	4898 (6)	1797 (15)	88 (10)
C(24)	11567 (15)	4660 (5)	3068 (15)	87 (10)
C(25)	11626 (14)	5080 (5)	4146 (14)	74 (9)
C(26)	11412 (12)	5757 (5)	3938 (12)	52 (8)

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