

The Structure of Methyl 2-[Benzyl(phenyl)phosphinyl]-1,2,3,4-tetrahydro-1-phenanthrenecarboxylate, an Intermediate in Phosphasteroid Synthesis

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Abstract. $C_{29}H_{27}O_3P$, $M_r = 454.51$, monoclinic, $P2_1/c$, $a = 21.683$ (4), $b = 5.625$ (1), $c = 21.189$ (3) Å, $\beta = 114.61$ (1)°, $V = 2349.8$ Å³, $Z = 4$, $D_o = 1.274$ (by flotation), $D_c = 1.284$ Mg m⁻³, $F(000) = 984$. The structure was solved by direct methods and refined by full-matrix and block-diagonal least squares to final R and R_w of 0.095 and 0.061, respectively, for 3157 intensities recorded on a diffractometer with Cu $K\alpha$ radiation. The flat fragment of the molecule is perpendicular to the [010] direction. The benzyl(phenyl)phosphinyl and carboxyl groups are in the *trans* position with a P–C–C–COOCH₃ torsion angle of 89.1 (3)°; their repulsive interaction forces a C(3) sofa conformation on the cyclohexene ring.

Introduction. In recent years Bodalski and co-workers have worked out syntheses of optically active 17-phosphasteroids. One of the intermediates of such a synthesis before the five-membered ring (*D*) closure is the title compound (Bodalski, Koszuk, Krawczyk & Pietrusiewicz, 1980). Configurations and structures of some other intermediates and model substances in phosphasteroid synthesis have already been studied by X-ray methods in our laboratory (Galdecki, 1979; Galdecki, Głowska, Bodalski & Pietrusiewicz, 1979; Galdecki & Głowska, 1980; Galdecki, Głowska & Goliński, 1981).

Colourless, transparent, needle-like crystals of the title compound were kindly supplied by Dr H. Krawczyk (Institute of Organic Chemistry, Technical University of Łódź). Intensities from an irregular crystal of approximate dimensions 0.20 × 0.36 × 0.15 mm were collected on a Syntex diffractometer with graphite-monochromated Cu radiation to a maximum of 116°. The total number of independent reflections measured was 3157, 166 of which had $|F_o| \leq 2\sigma(F_o)$. The intensities were not corrected for absorption ($\mu = 1.25$ mm⁻¹).

The structure was solved by *MULTAN* (Germain, Main & Woolfson, 1971). The *E* map based on 400 $E \geq 1.49$ ($R = 32.5\%$) enabled us to locate all but five of the non-hydrogen atoms. Their positions were found from Fourier syntheses. The structure was refined by full-matrix (isotropic, four cycles, $R = 0.146$, $R_w =$

0.124) and block-diagonal (anisotropic) least squares. H atom positions were calculated geometrically (*XANADU*) after three cycles of refinement of the P, O and C atoms with anisotropic thermal parameters ($R = 0.132$, $R_w = 0.115$) and refined in two isotropic full-matrix cycles. The final conventional and weighted agreement factors were 0.092 and 0.061, respectively, after three successive cycles of block-diagonal refine-

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

$$B_{iso} = \frac{1}{3}\pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	B_{iso} (Å ²)
P	7621 (1)	8612 (2)	1160 (1)	3.63 (5)
O(1)	7654 (1)	11176 (4)	997 (1)	4.6 (1)
O(2)	7138 (1)	7378 (5)	2775 (1)	6.0 (1)
O(3)	7555 (1)	11042 (4)	2857 (1)	6.2 (1)
C(1)	6768 (1)	9900 (6)	1755 (1)	3.6 (1)
C(2)	6859 (1)	7910 (5)	1299 (1)	3.7 (2)
C(3)	6229 (2)	7724 (6)	600 (2)	4.4 (2)
C(4)	5602 (2)	7129 (6)	730 (2)	4.9 (2)
C(5)	4280 (2)	7783 (6)	817 (2)	5.1 (2)
C(6)	3660 (2)	8174 (7)	830 (2)	5.8 (2)
C(7)	3551 (2)	10094 (7)	1198 (2)	5.3 (2)
C(8)	4070 (2)	11583 (6)	1559 (2)	4.7 (2)
C(9)	5285 (2)	12673 (6)	1984 (2)	5.2 (2)
C(10)	5924 (2)	12200 (6)	2034 (2)	4.8 (2)
C(11)	6034 (1)	10306 (6)	1647 (1)	3.9 (2)
C(12)	5501 (1)	8944 (5)	1212 (5)	3.6 (2)
C(13)	4838 (1)	9318 (5)	1193 (1)	3.8 (2)
C(14)	4731 (2)	11217 (6)	1574 (2)	4.3 (2)
C(15)	7157 (2)	9225 (6)	2512 (2)	4.7 (2)
C(20)	7614 (2)	6662 (6)	480 (1)	3.7 (2)
C(21)	8254 (2)	6925 (6)	366 (1)	4.1 (2)
C(22)	8349 (2)	8936 (6)	37 (2)	4.8 (2)
C(23)	8947 (2)	9193 (7)	-60 (2)	6.0 (2)
C(24)	9447 (2)	7479 (7)	179 (2)	5.7 (2)
C(25)	9356 (2)	5520 (7)	512 (2)	6.4 (2)
C(26)	8764 (2)	5220 (7)	612 (2)	5.3 (2)
C(30)	7946 (2)	10613 (9)	3619 (2)	8.6 (3)
C(31)	8348 (1)	7712 (6)	1932 (1)	3.8 (2)
C(32)	8905 (2)	9206 (6)	2169 (2)	5.2 (2)
C(33)	9498 (2)	8531 (7)	2754 (2)	6.7 (2)
C(34)	9509 (2)	6422 (7)	3091 (2)	6.2 (2)
C(35)	8949 (2)	4911 (6)	2855 (2)	5.8 (2)
C(36)	8369 (2)	5555 (6)	2269 (2)	5.3 (2)

ment of the non-hydrogen atoms with anisotropic thermal parameters.* The weights were $w^{-2} = \sigma(F)$. Neutral-atom scattering factors for P, O and C were those given by Doyle & Turner (1968) and those from *International Tables for X-ray Crystallography* (1962) for H atoms. All calculations were performed using the XRAY 70 system (Stewart, Kundell & Baldwin, 1970) and *MULTAN* (Germain, Main & Woolfson, 1971), on RIAD32 and RIAD22 computers.

Atomic coordinates are given in Table 1.

Discussion. The molecules are packed in the crystal almost perpendicular to [010], as was expected considering the short *b* axis and the planarity of a considerable fragment of the molecule (Fig. 1). The shortest intermolecular distances are 3.483 (5) Å for C(8)⋯O(2) ($1-x, 0.5+y, 0.5-z$), 3.501 (4) and 3.508 (5) Å for C(32)⋯C(35) and O(1)⋯C(36) ($x, 1+y, z$), which is indicative of fairly loose packing. The bond lengths and valency angles summarized in Tables 2 and 3 confirm crystallochemical regularities observed previously in compounds containing analogous groups. The bond distances in the naphthalene system are generally those expected from a consideration of resonance hybrids (Pauling, 1973) with mean values of 1.369 and 1.424 Å for 'shorter' and 'longer' bonds, respectively. The angles in this fragment generally do not differ from 120° by more than 3σ, but C(1)–C(11)–C(10) and C(1)–C(11)–C(12) deviate by –3.9 and 3.4°, probably because of a repulsive interaction between the benzyl(phenyl)phosphinyl and carboxyl substituents. The groups are *trans* with respect to each other with a P–C–COOCH₃ torsion angle of 89.1 (3)°. The C(11)–C(1)–C(15) angle of 106.3 (3)° and the non-chair conformation of

* Lists of structure factors, anisotropic thermal parameters and H atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35584 (17 pp.). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

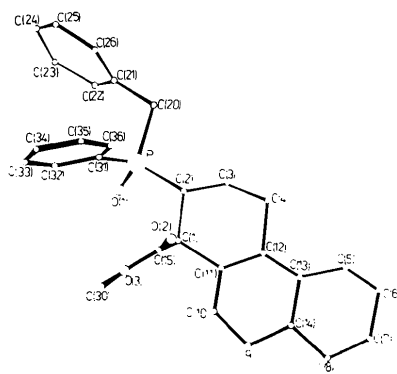


Fig. 1. View of the molecule normal to the naphthalene system showing the atom numbering.

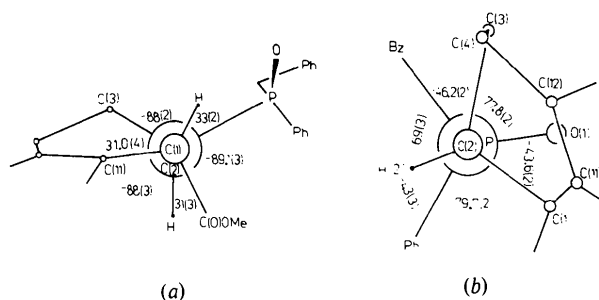


Fig. 2. Newman projections of the molecule viewed in the direction of the (a) C(1)–C(2) and (b) C(2)–P bonds. (Angles are in degrees.)

Table 2. Bond lengths (Å)

P–O(1)	1.492 (2)	C(9)–C(10)	1.370 (5)
P–C(2)	1.839 (4)	C(10)–C(11)	1.424 (5)
P–C(20)	1.806 (3)	C(11)–C(12)	1.374 (4)
P–C(31)	1.807 (3)	C(12)–C(13)	1.436 (5)
O(2)–C(15)	1.187 (4)	C(13)–C(14)	1.414 (5)
O(3)–C(15)	1.341 (4)	C(20)–C(21)	1.511 (5)
O(3)–C(30)	1.499 (5)	C(21)–C(22)	1.388 (5)
C(1)–C(2)	1.543 (5)	C(21)–C(26)	1.390 (5)
C(1)–C(11)	1.528 (5)	C(22)–C(23)	1.403 (6)
C(1)–C(15)	1.518 (4)	C(23)–C(24)	1.380 (5)
C(2)–C(3)	1.546 (4)	C(24)–C(25)	1.366 (6)
C(3)–C(4)	1.532 (5)	C(25)–C(26)	1.397 (6)
C(4)–C(12)	1.524 (5)	C(31)–C(32)	1.383 (5)
C(5)–C(6)	1.376 (5)	C(31)–C(36)	1.400 (5)
C(5)–C(13)	1.428 (4)	C(32)–C(33)	1.418 (4)
C(6)–C(7)	1.408 (6)	C(33)–C(34)	1.380 (6)
C(7)–C(8)	1.356 (5)	C(34)–C(35)	1.392 (5)
C(8)–C(14)	1.434 (5)	C(35)–C(36)	1.398 (4)
C(9)–C(14)	1.415 (4)		

Table 3. Valency angles (°)

O(1)–P–C(2)	112.2 (1)	C(5)–C(13)–C(12)	122.1 (3)
O(1)–P–C(20)	112.8 (1)	C(5)–C(13)–C(14)	118.2 (3)
O(1)–P–C(31)	111.9 (1)	C(12)–C(13)–C(14)	119.6 (3)
C(2)–P–C(20)	106.7 (1)	C(8)–C(14)–C(9)	121.0 (3)
C(2)–P–C(31)	107.3 (2)	C(8)–C(14)–C(13)	119.7 (3)
C(20)–P–C(31)	105.5 (1)	C(9)–C(14)–C(13)	119.2 (3)
C(15)–O(3)–C(30)	114.2 (3)	O(2)–C(15)–O(3)	123.5 (3)
C(2)–C(1)–C(11)	114.3 (2)	O(2)–C(15)–C(1)	127.1 (3)
C(2)–C(1)–C(15)	108.7 (2)	O(3)–C(15)–C(1)	109.4 (3)
C(11)–C(1)–C(15)	106.3 (3)	P–C(20)–C(21)	111.4 (2)
P–C(2)–C(1)	107.6 (2)	C(20)–C(21)–C(22)	119.8 (3)
P–C(2)–C(3)	110.8 (2)	C(20)–C(21)–C(26)	120.8 (3)
C(1)–C(2)–C(3)	110.9 (2)	C(22)–C(21)–C(26)	119.4 (3)
C(2)–C(3)–C(4)	109.8 (3)	C(21)–C(22)–C(23)	119.8 (3)
C(3)–C(4)–C(12)	111.2 (3)	C(22)–C(23)–C(24)	120.5 (4)
C(6)–C(5)–C(13)	120.0 (3)	C(23)–C(24)–C(25)	119.5 (4)
C(5)–C(6)–C(7)	121.6 (3)	C(24)–C(25)–C(26)	121.0 (3)
C(6)–C(7)–C(8)	119.7 (3)	C(21)–C(26)–C(25)	119.8 (3)
C(7)–C(8)–C(14)	120.7 (3)	P–C(31)–C(32)	117.3 (2)
C(10)–C(9)–C(14)	120.5 (3)	P–C(31)–C(36)	122.4 (2)
C(9)–C(10)–C(11)	120.5 (3)	C(32)–C(31)–C(36)	120.2 (2)
C(1)–C(11)–C(10)	116.1 (2)	C(31)–C(32)–C(33)	119.5 (3)
C(1)–C(11)–C(12)	123.4 (3)	C(32)–C(33)–C(34)	119.7 (3)
C(10)–C(11)–C(12)	120.4 (3)	C(33)–C(34)–C(35)	121.0 (3)
C(4)–C(12)–C(11)	120.4 (3)	C(34)–C(35)–C(36)	119.2 (3)
C(4)–C(12)–C(13)	120.1 (2)	C(31)–C(36)–C(35)	120.3 (3)
C(11)–C(12)–C(13)	119.4 (3)		

the cyclohexene ring are caused by the same effect. The distortions observed in the P atom tetrahedron are typical for a phosphoryl compound, *i.e.* O=P—C valency angles increase to 112–113° while C—P—C angles decrease to 106–107°. The cyclohexene ring adopts a C(3)-sofa conformation flattened at the C(11) end. The asymmetry parameters (Duax & Norton, 1975) are: $\Delta C_s^3 = 6.3$ (4), $\Delta C_2^{2,3} = 25.0$ (4), $\Delta C_s^{1,2} = 52.5$ (4) and $\bar{\varphi} = 30.2$ (4)°.

Newman projections about the C(1)—C(2) and C(2)—P bonds are shown in Fig. 2.

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(±)-2-(2-Chlorophenoxy)propionic Acid

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Abstract. C₉H₉ClO₃, *M_r* = 200.6, monoclinic, *P*2₁/*n*, *a* = 7.400 (2), *b* = 7.913 (4), *c* = 16.495 (5) Å, β = 93.16 (2)°, *D_c* = 1.38 Mg m⁻³, *Z* = 4, *F*(000) = 416, μ(Mo *K*α) = 0.37 mm⁻¹. The structure was solved by direct methods and refined to a final *R* = 0.041 for 1007 observed reflexions. The molecules form centrosymmetric hydrogen-bonded cyclic dimers (O...O, 2.626 Å) and adopt the synclinal conformation found for all known phenoxypropionic acids.

Introduction. The title compound was first prepared by Synerholm & Zimmerman (1945), who found its useful herbicidal properties to be similar to those of the acetic

acid homologue. Although the crystal structures of a number of 2-phenoxypropionic acid analogues are now known, including the parent acid, 2-phenoxypropionic acid (Kennard, Smith & White, 1980), 2-(3,5-dichlorophenoxy)propionic acid (Smith, Kennard & White, 1978), 2-(2,4,5-trichlorophenoxy)propionic acid (Smith, Kennard, White & Hodgson, 1977) and 2-(4-chloro-2-methylphenoxy)propionic acid (Smith, Kennard, White & Hodgson, 1980), the structure of the title compound was determined as a check on the predictions of Smith *et al.* (1980) regarding preferred conformations in the propionic acids. In the case of 2-chlorophenoxyacetic acid (Chandrasekhar & Pat-