Crystal Structure and Conformation of Methyl 2-Methyl-3-[benzyl(phenyl)phosphinyl]butyrate

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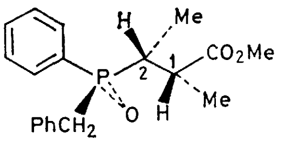
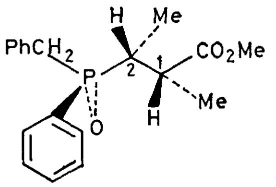
The structure of one of the diastereoisomeric methyl 2-methyl-3-[benzyl(phenyl)phosphinyl]butyrates has been determined by *X*-ray diffraction. Crystals are orthorhombic, space group *Pcab*, with the cell constants a = 10.738(3), b = 12.800(3), and c = 26.503(3) Å, Z = 8. The structure was determined by direct methods and refined to R 7.8% for 1 783 intensities. The molecule has a *threo*-configuration; it prefers a conformation with *gauche* methine hydrogens and reasons for this are suggested.

A CONJUGATE addition of s-phosphine oxides to α,β-unsaturated carboxylic esters affording t-β-carboxyethylphosphine oxides has recently been utilised as the first step in a one-pot synthesis of a variety of heterocycles containing a phosphorus atom incorporated into a five-membered ring.[1] For the sake of consecutive stereochemical studies [2] a series of β-methoxycarbonylethylphosphine oxides was synthesized and analysed by means of ^{1}H, ^{31}P, and ^{13}C n.m.r. spectroscopy from the configurational and conformational point of view. Although the majority of the obtained data could be unequivocally interpreted, some appeared insufficient for final structural conclusions to be made.

The addition of benzyl(phenyl)phosphine oxide to methyl 2-methylcrotonate resulted in the selective formation of two of four theoretically possible diastereoisomeric adducts. For one of them [(1a); m.p. 153—155 °C; δ ^{31}P 42.3 p.p.m.] the *threo*-configuration of the ethane fragment was assigned [2] on the basis of ^{3}J(H-1, H-2) 3.5 Hz and ^{3}J(P-CO) 16 Hz. These values also indicate an unexpectedly high population of the conformer with *gauche* vicinal hydrogens [3a,b] and *anti*-phosphoryl and carbonyl groups.[2,4] For the other adduct [(1b); m.p. 146—147 °C; δ ^{31}P 43.5 p.p.m.] an analogous relative configuration and conformation around C(1)-C(2) bond could be suggested by the value for ^{3}J(P-CO) of 16 Hz and the similarity of the ^{13}C n.m.r. spectra of both diastereoisomers.[2] Unfortunately, the methine protons H-1 and H-2 of this compound turned out to be accidentally equivalent [3c] and coupling between them is not manifested in the ^{1}H n.m.r. spectrum. Lack of this strongly diagnostic parameter lessens significantly the certainty of the suggested assignment. Furthermore, a ^{3}J(H'-D) coupling constant found for (1b) deuteriated at C-2 to be <0.5 Hz and indicating *gauche* nuclei cannot be regarded as being completely reliable.[5]



(1a)



(1b)

In order to identify unquestionably the configuration and conformation of (1b) and possibly disclose the factors imposing the unexpected conformational preference for gauche hydrogens, the crystal structure was determined.

RESULTS AND DISCUSSION

Figure 1 shows a view of a molecule of compound (1b) along [100] together with the crystallographic atom numbering system used [C-1, C-2, H-1, and H-2 are numbered C(7), C(8), H(7), and H(8)]. The Figure shows the *threo*-configuration in the ethane fragment, the same as has previously been found for (1a).

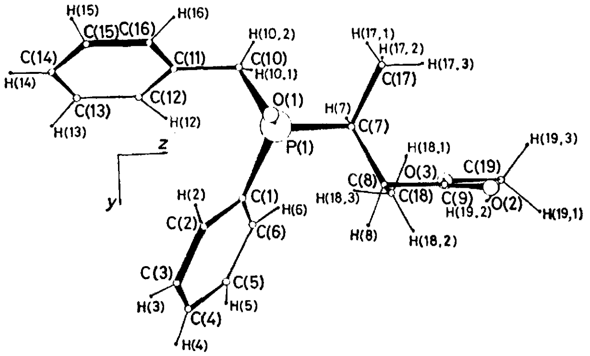


FIGURE 1 The molecule of (1b) viewed along [100] showing the crystallographic atom numbering system

Bond lengths, bond angles, and final co-ordinates of the non-hydrogen atoms are given in Tables 1—3.

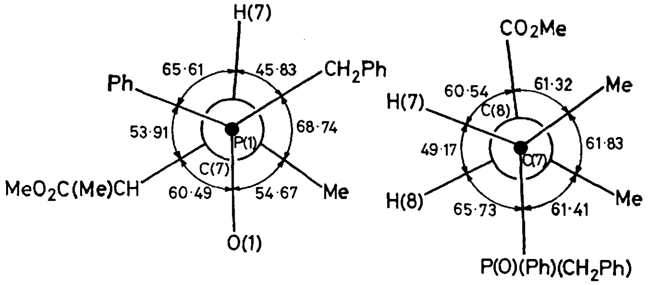


FIGURE 2 Newman projections of the molecule viewed in the direction of the P(1)–C(7) and C(7)–C(8) bonds

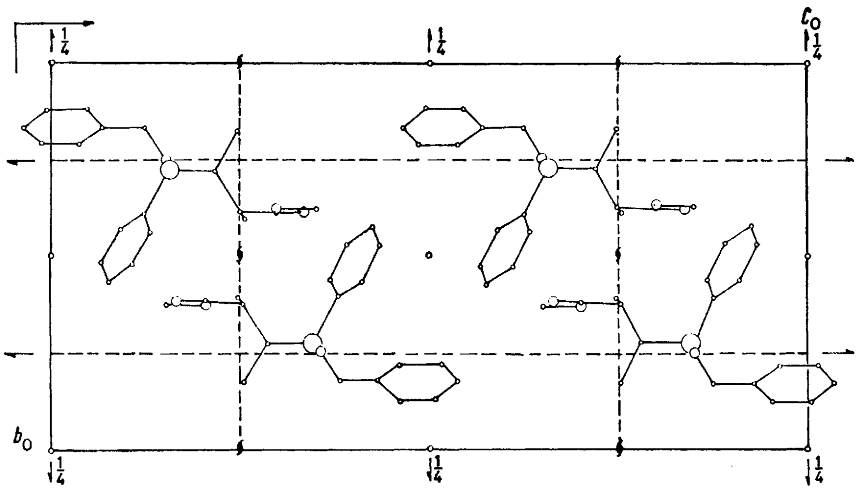


FIGURE 3 Packing of molecules in the unit cell: only half the molecules are shown for clarity

Dihedral angles are quoted in Figure 2 and Figure 3 shows the molecular packing in the unit cell.

The vast majority of these data represent values close to those commonly observed and therefore do not need to be discussed in detail. Also, all intermolecular and intramolecular distances between non-bonded atoms are close to or greater than the pertinent sums of van der Waals radii. Some indicative examples are given in Table 4. However, some of the bond angles are significantly distorted, showing an accommodation of the interactions from which the molecule suffers most. This relates to the 1,3-interaction between the phosphoryl oxygen and C-2 methyl group and the *gauche* interaction of the methyl groups as shown in Figure 4. In order to minimize the interactions bond-angle spreadings have occurred, resulting in an O(1)–P–C(7) angle of 113.72° and a C(7)–C(8)–C(18) angle of 115.97°. These angles cause the moving of phosphoryl oxygen and the C(18) methyl away from one another (Figure 4). A similar bond-angle enlargement causes C(8)–C(7)–C(17) to be 113.82°, in order that the C(17) methyl may move further away from C(18) methyl group.

TABLE 1

Bond lengths (Å) for non-hydrogen atoms, with estimated standard deviations in parentheses

P–O(1)	1.491(2)	C(8)–C(9)	1.509(5)
P–C(1)	1.813(3)	C(8)–C(18)	1.546(5)
P–C(7)	1.841(3)	C(9)–O(2)	1.208(4)
P–C(10)	1.839(3)	C(9)–O(3)	1.310(5)
C(1)–C(2)	1.401(4)	C(10)–C(11)	1.498(4)
C(2)–C(3)	1.403(5)	C(11)–C(12)	1.395(5)
C(3)–C(4)	1.420(6)	C(12)–C(13)	1.401(5)
C(4)–C(5)	1.389(6)	C(13)–C(14)	1.362(6)
C(5)–C(6)	1.380(5)	C(14)–C(15)	1.423(6)
C(6)–C(1)	1.399(4)	C(15)–C(16)	1.428(5)
C(7)–C(8)	1.544(5)	C(16)–C(11)	1.406(5)
C(7)–C(17)	1.554(5)	C(19)–O(3)	1.483(4)

TABLE 2

Valency angles (°) for non-hydrogen atoms, with estimated standard deviations in parentheses

O(1)–P–C(1)	112.51(13)	C(7)–C(8)–C(9)	107.49(26)
O(1)–P–C(7)	113.72(13)	C(7)–C(8)–C(18)	115.97(27)
O(1)–P–C(10)	113.14(14)	C(8)–C(7)–C(17)	113.82(24)
C(1)–P–C(7)	107.38(14)	C(8)–C(9)–O(2)	124.26(34)
C(1)–P–C(10)	105.49(14)	C(8)–C(9)–O(3)	115.21(27)
C(7)–P–C(10)	103.86(14)	C(9)–C(8)–C(18)	109.70(27)
P–C(1)–C(2)	116.76(23)	C(9)–O(3)–C(19)	116.28(26)
P–C(1)–C(6)	121.66(23)	O(2)–C(9)–O(3)	120.52(30)
P–C(7)–C(8)	110.53(20)	C(10)–C(11)–C(12)	118.95(28)
P–C(7)–C(17)	109.15(22)	C(10)–C(11)–C(16)	120.38(28)
P–C(10)–C(11)	110.61(22)	C(11)–C(12)–C(13)	121.02(33)
C(1)–C(2)–C(3)	118.22(32)	C(12)–C(13)–C(14)	119.22(37)
C(2)–C(3)–C(4)	119.53(35)	C(13)–C(14)–C(15)	121.74(37)
C(3)–C(4)–C(5)	121.09(35)	C(14)–C(15)–C(16)	119.02(36)
C(4)–C(5)–C(6)	119.26(34)	C(15)–C(16)–C(11)	118.31(34)
C(5)–C(6)–C(1)	120.32(31)	C(16)–C(11)–C(12)	120.66(30)
C(6)–C(1)–C(2)	121.55(29)		

TABLE 3

Final co-ordinates of non-hydrogen atoms (× 10^4) with estimated standard deviations in parentheses

Atom	x	y	z
P(1)	5 195(1)	2 701(1)	1 550(1)
O(1)	6 561(2)	2 507(2)	1 515(1)
O(2)	5 012(3)	3 822(3)	3 379(1)
O(3)	3 225(2)	3 724(2)	2 985(1)
C(1)	4 735(3)	3 912(2)	1 248(1)
C(2)	5 592(3)	4 359(3)	913(1)
C(3)	5 260(4)	5 290(3)	668(1)
C(4)	4 075(4)	5 742(3)	762(2)
C(5)	3 236(3)	5 277(3)	1 092(1)
C(6)	3 566(3)	4 362(3)	1 333(1)
C(7)	4 604(3)	2 739(3)	2 202(1)
C(8)	5 047(3)	3 741(3)	2 472(1)
C(9)	4 444(4)	3 761(3)	2 986(1)
C(10)	4 255(3)	1 677(3)	1 247(1)
C(11)	4 455(3)	1 679(3)	688(1)
C(12)	3 558(3)	2 138(3)	378(1)
C(13)	3 682(4)	2 125(3)	−148(1)
C(14)	4 711(4)	1 681(3)	−358(1)
C(15)	5 657(4)	1 213(3)	−57(2)
C(16)	5 522(3)	1 213(3)	479(1)
C(17)	4 982(3)	1 714(3)	2 477(1)
C(18)	6 471(3)	3 872(3)	2 527(1)
C(19)	2 611(4)	3 714(4)	3 487(1)

TABLE 4

The smallest intermolecular distances (Å)

O(1) · · · $C(6^{I})$	3.254(4)	O(2) · · · $C(14^{II})$	2.421(5)
O(1) · · · $C(10^{I})$	3.157(4)	C(15) · · · $C(15^{III})$	3.424(5)

I $\frac{1}{2} + x, \frac{1}{2} - y, z$ II $1 - x, \frac{1}{2} - y, \frac{1}{2} + z$
III $1 - x, -y, -z$

Another interesting feature of compounds (1a) and (1b) is their preferred conformation with *gauche* hydrogens in the ethane fragment either in solution ($CDCl_3$) or in the solid state. This rather unexpected preference cannot be assumed to be due to the repulsive steric interactions between the geminal substituents at C-1 and C-2 analogous to those recently found for other tetrasubstituted ethanes.[6] The data collected in Table 2 do not provide the necessary confirmation of bond-angle spreading connected implicitly with such interactions.[6] The pertinent values for bond angles of (1b), namely 109.15° for P–C(7)–C(17) and 109.70° for C(9)–C(8)–C(18) are very close to tetrahedral.

We suggest that the observed *gauche* conformation is an ultimate result of an energy minimization process and is explicable in terms of 1,3- and 1,2-interactions. This point will be discussed in detail elsewhere.[2]

The attractive interactions of the phosphoryl and carbonyl groups with proximal hydrogen, recently invoked in β-ketophosphine oxides [7] in order to rationalize the preference of the conformation with *trans*-vicinal hydrogens, do not occur in the phosphine oxide (1b), in spite of the strikingly close resemblance of the systems.

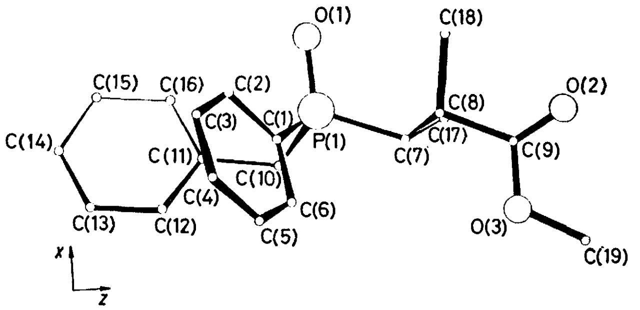


FIGURE 4 1,3-Interaction between phosphoryl oxygen O(1) and the C-2 methyl group C(18)

EXPERIMENTAL

The adduct (1b) was available from another study [2] and was recrystallized from chloroform.

Preliminary Weissenberg, oscillation, and KFOR-retigraph photographs established space group *Pcab*. Intensities were collected from an unshaped crystal on a Syntex $P2_1$ four-circle diffractometer by use of graphite-monochromated Cu-K_α radiation. Measurements were carried out in the θ—2θ mode ($2\theta < 110°$). Of 2 317 recorded reflections, 1 783 having $|F| \geqslant 2\sigma(F)$ were considered observed. Lorentz and polarization (Lp) corrections were applied.

Crystal Data.—$C_{19}H_{23}O_3P$, $M = 330.37$. Orthorhombic, $a = 10.738(3)$, $b = 12.800(3)$, $c = 26.503(5)$ Å, $U = 3\,642.74$ Å^3, D_m(flotation) $= 1.194$, $Z = 8$, $D_c = 1.204$ g cm^{-3}. Space group *Pcab*. Cu-K_α radiation, $\lambda = 1.541\,78$ Å; μ(Cu-K_α) $= 14.2$ cm^{-1}.

Structure Solution and Refinement.—The structure was solved by the multisolution technique by use of MULTAN,[8] and based on $338E \geqslant 1.5$. An E map showed the position of 15 out of the 23 non-hydrogen atoms, and the remaining 8 atoms were located by Fourier synthesis. A structure-factor calculation based on those positions yielded R 26%. After six cycles of full-matrix least-squares with isotropic thermal parameters and a further six cycles of block-diagonal refinement with anisotropic thermal parameters R was 11.3% (R' 9.6%). A difference-Fourier map revealed the positions of all 23 hydrogen atoms which were refined in two isotropic cycles. Finally, two cycles of block-diagonal least-squares refinement (hydrogen atoms with isotropic, others with anisotropic temperature factors) reduced R to 7.8% and R' to 6.3%.

Hydrogen atom parameters, anisotropic thermal parameters for non-hydrogen atoms, and final observed and calculated structure factors are listed in Supplemenatry Publication No. SUP 22568 (17 pp.).* Neutral scattering factors were taken from ref. 9 for hydrogen atoms and from ref. 10 for non-hydrogen atoms. Calculations were performed on a RIAD computer by use of the 'X-Ray '70' program system.[11]

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin II*, 1978, Index issue.