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### Structure of (*Z*)-3-Ethoxycarbonyl-4-phenyl-3-pentenoic acid, C<sub>14</sub>H<sub>16</sub>O<sub>4</sub>\*

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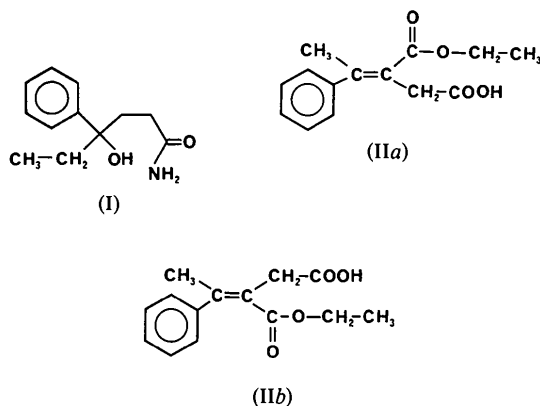
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**Abstract.**  $M_r = 248.3$ , orthorhombic, *Pbcn*,  $a = 35.934$  (5),  $b = 7.502$  (2),  $c = 10.056$  (2) Å,  $V = 2711$  (2) Å<sup>3</sup>,  $Z = 8$ ,  $D_x = 1.22$  Mg m<sup>-3</sup>,  $Cu K\alpha$ ,  $\lambda = 1.5418$  Å,  $\mu = 0.697$  mm<sup>-1</sup>,  $F(000) = 1056$ ,  $T = 293$  K, final  $R = 0.050$  for 1600 observed reflections. The X-ray study confirms that in the solid state the structure of the *Z* isomer is similar to that inferred on the basis of chemical and spectroscopic evidence. In the crystal the title compound has a non-planar conformation and forms centrosymmetric hydrogen-bonded dimers, O...O distance 2.690 (3) Å, O—H...O angle 171 (2)°. There is no conjugation between the phenyl ring and the C(3) double bond.

**Introduction.** As a part of our studies regarding the total synthesis of compounds with anticonvulsant activity, we became interested in designing a synthetic entry into the  $\gamma$ -hydroxy,  $\gamma$ -phenyl caproamide (Carvajal, Russek, Tapia & Massieu, 1964; Pérez de la Mora & Tapia, 1973; Joseph-Nathan, Massieu, Carvajal & Tapia, 1978), molecule (I). Careful analysis of the structural features characteristic of this anticonvulsant molecule suggests the utilization of (II) as a versatile intermediate for this synthesis. The (*E* and *Z*) geometric isomers of (II) were obtained from the condensation of acetophenone with diethyl succinate at alkaline pH

(Stobbe, 1899). Both isomers (IIa, IIb) were characterized on the basis of chemical and spectroscopic methods (García, 1983).



It was of interest to study the crystallographic structure of the *Z* isomer (IIb) in order to ascertain its conformation and to obtain further information concerning its molecular geometry.

**Experimental.** Cubic shaped crystal 0.36 × 0.36 × 0.38 mm, Nicolet R3 four-circle diffractometer, graphite-monochromated  $Cu K\alpha$ , lattice parameters from 15 machine-centred reflections with  $4.9 < 2\theta < 26.2^\circ$ ; 2079 reflections with  $3 < 2\theta < 115^\circ$  for an

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octant, 1600 independent with  $I > 2.5\sigma(I)$ , index range  $h$  0/38,  $k$  0/7,  $l$  0/10,  $\omega$ -scan mode, variable scan speed, scan width  $1.0^\circ(\theta)$ , two standard reflections monitored every 50 measurements, Lp correction, absorption ignored; structure solved by direct methods using *SHELXTL* (Sheldrick, 1981); least-squares refinement of all non-H atoms treated anisotropically, H atoms riding on the bonded C with a fixed isotropic temperature factor  $U = 0.06 \text{ \AA}^2$ , coordinates of H atom of hydroxyl group refined; function minimized  $\sum w(\Delta F)^2$ ,  $w = |\sigma^2(F_o) + 0.00178(F_o)^2|^{-1}$ ,  $(\Delta/\sigma)$  max.  $< 0.05$ ; residual electron density within  $\pm 0.2 e \text{ \AA}^{-3}$ ; isotropic extinction parameter  $X = 0.0016$ ; final  $R = 0.050$ ,  $wR = 0.084$ ; scattering factors from *International Tables for X-ray Crystallography* (1974).

**Discussion.** A perspective molecular drawing of the *Z* isomer is shown in Fig. 1. Final atomic coordinates are in Table 1\* and bond distances and angles in Table 2. The average e.s.d. for bond lengths is  $0.003 \text{ \AA}$  and for bond angles  $0.2^\circ$ .

In all essential details, the molecular geometry of (IIb) in terms of the bond lengths and angles shows normal values. However, the bond length C(4)–C(7) =  $1.522(3) \text{ \AA}$  is significantly longer than the standard  $Csp^2-Csp^2$  single-bond length (Sutton, 1965), indicating that there is no conjugation of the C(3)–C(4) methylene bond with the phenyl ring.

\* Lists of structure amplitudes, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42083 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

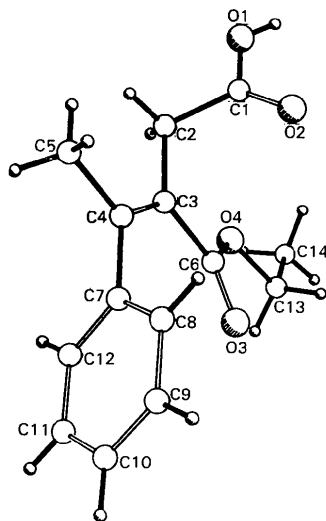


Fig. 1. Projection of the molecule of (*Z*)-3-ethoxycarbonyl-4-phenyl-3-pentenoic acid, showing the atom labelling.

The maximum deviation from the mean plane through the atoms C(7)–C(12) of the phenyl ring is  $0.009(3) \text{ \AA}$ . The mean plane through the atoms C(3), C(4), C(6), C(7), C(13), C(14), O(3), O(4) of the ethoxycarbonyl group shows a much larger deviation: maximum deviations from the plane are  $-0.219(3)$  and  $0.296(3) \text{ \AA}$  for O(3) and C(6), respectively. The dihedral angle between these two planes is  $80.0(4)^\circ$  also showing the impossibility of conjugation.

The pentenoic acid and ethoxycarbonyl groups are oriented to minimize transannular repulsions between their O atoms [O(4)···O(2)  $3.254(4) \text{ \AA}$ ]. Thus, the planes defined by C(1), C(2), C(3), C(4), O(1), O(2) and the ethoxycarbonyl group are nearly perpendicular at  $110.4(4)^\circ$ . The angle between the planes of the phenyl ring and the carboxyl group is only  $28.4(4)^\circ$ .

Table 1. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic temperature factors ( $\text{\AA}^2 \times 10^3$ ) for the non-hydrogen atoms

$$U_{eq} = (U_{11}U_{22}U_{33})^{1/3}.$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
O(1)	5242 (1)	6195 (2)	1344 (2)	60 (1)
O(2)	5433 (1)	4257 (2)	-239 (2)	61 (1)
O(3)	6209 (1)	789 (2)	749 (2)	73 (1)
O(4)	5828 (1)	2127 (2)	2202 (2)	54 (1)
C(1)	5494 (1)	5244 (3)	726 (2)	40 (1)
C(2)	5876 (1)	5530 (3)	1289 (2)	44 (1)
C(3)	6156 (1)	4126 (3)	815 (2)	43 (1)
C(4)	6455 (1)	4575 (3)	67 (2)	43 (1)
C(5)	6538 (1)	6500 (3)	-427 (3)	59 (1)
C(6)	6079 (1)	2176 (3)	1218 (2)	45 (1)
C(7)	6739 (1)	3187 (3)	-368 (2)	43 (1)
C(8)	7026 (1)	2665 (3)	467 (2)	49 (1)
C(9)	7298 (1)	1459 (4)	18 (3)	61 (1)
C(10)	7290 (1)	786 (4)	-1253 (3)	65 (1)
C(11)	7007 (1)	1299 (4)	-2085 (3)	74 (1)
C(12)	6735 (1)	2515 (4)	-1656 (2)	61 (1)
C(13)	5707 (1)	313 (3)	2666 (3)	65 (1)
C(14)	5435 (1)	575 (4)	3726 (3)	79 (1)

Table 2. Bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) with e.s.d.'s in parentheses

O(1)–C(1)	1.310 (3)	O(2)–C(1)	1.240 (3)
O(3)–C(6)	1.235 (3)	O(4)–C(6)	1.339 (3)
O(4)–C(13)	1.503 (3)	C(1)–C(2)	1.501 (3)
C(2)–C(3)	1.532 (3)	C(3)–C(4)	1.353 (3)
C(3)–C(6)	1.544 (3)	C(4)–C(5)	1.556 (3)
C(4)–C(7)	1.522 (3)	C(7)–C(8)	1.388 (3)
C(7)–C(12)	1.390 (3)	C(8)–C(9)	1.407 (3)
C(9)–C(10)	1.374 (4)	C(10)–C(11)	1.372 (4)
C(11)–C(12)	1.405 (4)	C(13)–C(14)	1.460 (4)
C(6)–O(4)–C(13)	116.7 (2)	O(1)–C(1)–O(2)	125.0 (2)
O(1)–C(1)–C(2)	112.0 (2)	O(2)–C(1)–C(2)	122.9 (2)
C(1)–C(2)–C(3)	112.6 (2)	C(2)–C(3)–C(4)	121.5 (2)
C(2)–C(3)–C(6)	116.9 (2)	C(4)–C(3)–C(6)	121.7 (2)
C(3)–C(4)–C(5)	124.1 (2)	C(3)–C(4)–C(7)	121.4 (2)
C(5)–C(4)–C(7)	114.5 (2)	O(3)–C(6)–O(4)	121.0 (2)
O(3)–C(6)–C(3)	129.0 (2)	O(4)–C(6)–C(3)	110.0 (2)
C(4)–C(7)–C(8)	121.3 (2)	C(4)–C(7)–C(12)	120.6 (2)
C(8)–C(7)–C(12)	117.9 (2)	C(7)–C(8)–C(9)	120.4 (2)
C(8)–C(9)–C(10)	121.3 (2)	C(9)–C(10)–C(11)	118.7 (2)
C(10)–C(11)–C(12)	120.7 (3)	C(7)–C(12)–C(11)	121.0 (2)
O(4)–C(13)–C(14)	107.4 (2)		

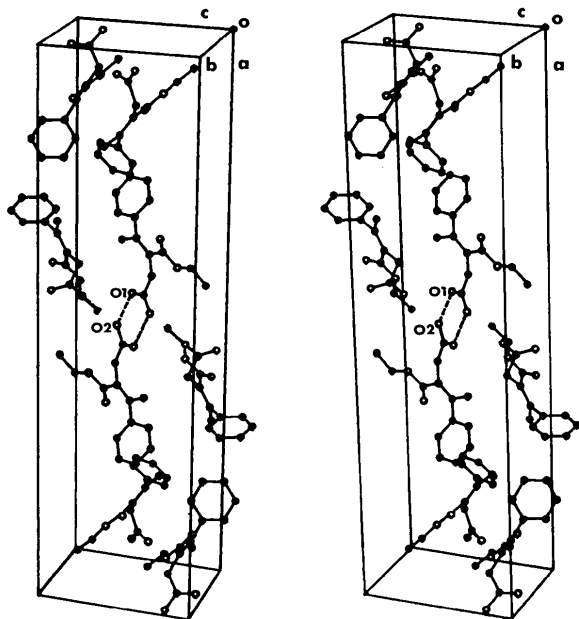


Fig. 2. Stereoscopic view of the unit cell showing the centrosymmetric hydrogen-bonded dimers.

Fig. 2 shows a stereoscopic view of the molecular packing. A hydrogen bond between the O(1) hydroxyl group and the O(2) carbonyl oxygen atoms of neighbouring molecules constitutes the major inter-

molecular attraction and packing force. The two molecules are linked by a pair of O(1)—H...O(2) hydrogen bonds across a crystallographic centre of inversion. The O(1)...O(2) and H(1)...O(2) distances are 2.690 (3) and 2.00 (3) Å, and the O(1)—H...O(2) angle is 171 (2)°.

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### Structure of *p*-Anisoïn, C<sub>16</sub>H<sub>16</sub>O<sub>4</sub>

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**Abstract.**  $M_r = 272.3$ ,  $P2_12_12_1$ ,  $a = 12.073$  (2),  $b = 18.917$  (2),  $c = 5.977$  (1) Å,  $V = 1365.1$  (4) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.325$  Mg m<sup>-3</sup>,  $\text{Cu } K\alpha$ ,  $\lambda = 1.5418$  Å,  $\mu = 0.74$  mm<sup>-1</sup>,  $F(000) = 576$ ,  $T = 295$  K, final  $R = 0.042$  for 1242 non-zero reflections. The hydrogen bond between the carbonyl O and hydroxyl O atoms in *p*-anisoïn is intramolecular [O...O 2.611 (3), H...O 2.01 (4) Å, O—H...O 113 (3), O=C—C—O 15.1 (4)°]. The molecular conformation is similar to that of benzoin, in which there is no intramolecular hydrogen bond. It has been shown that the type of hydrogen bond in solid benzoin depends on the molecular packing in the crystals.

**Introduction.** Previous work on benzoin (Haisa, Kashino & Morimoto, 1980) has shown that there is no intramolecular hydrogen bond between the carbonyl O and hydroxyl O atoms, in spite of an O...O distance of 2.585 (4) Å, but a bifurcated hydrogen bond exists between the intermolecular O atoms. Additionally, an IR spectrum (KBr disk) of *p*-anisoïn (1) shows a sharp singlet in the OH stretching frequency band at 3450 cm<sup>-1</sup>, while that of benzoin (2) shows a doublet at 3390 and 3350 cm<sup>-1</sup> (Suryanarayana & Subrahmanyam, unpublished). This difference in the IR spectrum suggests a difference in the type of hydrogen bond in (1) and (2). However, there is no systematic