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[4-(Benzyloxy)phenyl]acetic Acid, $C_{15}H_{14}O_3$

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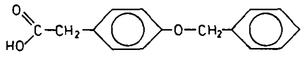
Abstract. $M_r = 242{\cdot}28$, triclinic, $P\bar{1}$, $a = 5{\cdot}487\,(3)$, $b = 8{\cdot}121\,(3)$, $c = 27{\cdot}424\,(8)$ Å, $\alpha = 89{\cdot}07\,(3)$, $\beta = 86{\cdot}65\,(3)$, $\gamma = 88{\cdot}98\,(4)°$, $V = 1220\,(1)$ Å^3, $Z = 4$, $D_x = 1{\cdot}319\,(1)$ g cm^{-3}, Mo $K\alpha$ radiation, graphite monochromator, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}85$ cm^{-1}, $F(000) = 512$, room temperature, $R(F) = 0{\cdot}045$ for 1798 independent reflections. Both independent molecules form centrosymmetric dimers *via* double hydrogen bonds through the carboxyl groups. The dihedral angles between the phenyl rings are 64·0 (3) and 64·1 (3)°. The two molecules differ in the relative orientations of the carboxyl groups, but are otherwise similar. The dimers are arranged in parallel stacks in the **c** direction.

Introduction. The title compound is one of several benzyloxy–phenyl–acetic acid derivatives and isomers that have been synthesized and studied to find new non-steroidal analgesics with antiphlogistic activity (Canenbley, 1983). So far the title compound has shown promising activity and low toxicity. To gain insight into the structure/activity relationship of this and related compounds, a crystal structure determination was undertaken.



Experimental. Synthesis by Canenbley (1983), colorless plates by recrystallization from ether, sample dimensions $0{\cdot}15 \times 0{\cdot}40 \times 0{\cdot}42$ mm, cell constants from setting angles of 25 reflections with $5 < \theta < 12°$, CAD-4 diffractometer, hemisphere up to $2\theta = 45°$, $(\sin\theta/\lambda)_{\max} = 0{\cdot}54$ Å^{-1}, ω scan, total number of reflections 2214, h 0–5, k −6–8, l ±29, independent reflections 1972; three standard reflections every 4500 s remained stable; no absorption correction, internal agreement of equivalent reflections $R_{\rm int} = 0{\cdot}01$, 1798 reflections with $I > 0{\cdot}3\sigma(I)$ used, $w(I) = 1/[\sigma^2(I) + (0{\cdot}03I)^2]$, structure determination by *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), H atoms of carboxyl groups from difference synthesis, those of carbon skeleton calculated, refinement on F, non-carboxyl H atoms refined but isotropic thermal parameters fixed, extinction parameter included [$g = 5\,(1) \times 10^{-7}$], two independent molecules refined in alternating cycles, final difference synthesis peaks $\leq 0{\cdot}22$ e Å^{-3}, max. $\Delta/\sigma = 0{\cdot}3$; $R = 0{\cdot}045$, $wR = 0{\cdot}046$, $S = 1{\cdot}88$, scattering factors from *International Tables for X-ray Crystallography* (1974), calculations performed with the *SDP* program system (Enraf–Nonius, 1982).

Discussion. The positional parameters are reported in Table 1,* the bond lengths and angles in Table 2, and the geometries of the two independent molecules are shown in Fig. 1. Both molecules form centrosymmetric dimers *via* hydrogen bonding by the carboxyl groups. The long dimers are arranged in parallel stacks in the crystallographic **c** direction (Fig. 2). There are no contacts between the dimers shorter than the sum of the van der Waals radii of the involved atoms.

The C—O bond lengths in the carboxyl group of molecule (I) differ by 0·036 (2) Å while those of molecule (II) are equal. This means that the H-atom positions in the hydrogen bonds are disordered. One would expect to find two H-atom positions in both O(1)···O(2′) and O(4)···O(5′) hydrogen bonds. However, owing to the experimental resolution only one maximum could be found. Consequently, the observed O—H distances are unrealistic. The O(1)···O(2′) distance of 2·697 (2) Å and the O(4)···O(5′) distance of 2·639 (2) Å correspond to hydrogen bonds of intermediate strength. The relevant torsion angles describing the molecular conformation are given in Table 3.

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* Lists of anisotropic thermal parameters, hydrogen-atom coordinates and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39205 (13 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 and equivalent values of anisotropic thermal parameters*

$$B_{\rm eq} = \tfrac{4}{3}\textstyle\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$(Å^2)
O(1)	0·7524 (4)	0·0567 (3)	0·02679 (7)	5·36 (5)
O(2)	0·3768 (3)	0·1501 (3)	0·04285 (7)	5·10 (5)
O(3)	0·5540 (3)	0·0588 (2)	0·28015 (6)	4·14 (4)
C(1)	0·6054 (5)	0·1515 (3)	0·04837 (9)	3·34 (6)
C(2)	0·6940 (5)	0·2738 (3)	0·08354 (9)	3·70 (7)
C(3)	0·6601 (4)	0·2138 (3)	0·13577 (8)	2·98 (6)
C(4)	0·4569 (5)	0·2597 (4)	0·16493 (9)	3·75 (7)
C(5)	0·4287 (5)	0·2064 (4)	0·21238 (9)	3·82 (7)
C(6)	0·6018 (4)	0·1053 (3)	0·23229 (9)	3·04 (6)
C(7)	0·8047 (4)	0·0590 (3)	0·20420 (9)	3·42 (6)
C(8)	0·8315 (5)	0·1144 (3)	0·15658 (9)	3·57 (7)
C(9)	0·7267 (5)	−0·0457 (4)	0·3027 (1)	4·06 (7)
C(10)	0·6272 (5)	−0·0884 (3)	0·35304 (9)	3·41 (6)
C(11)	0·4183 (5)	−0·1770 (4)	0·3605 (1)	4·38 (7)
C(12)	0·3327 (5)	−0·2204 (4)	0·4072 (1)	5·14 (8)
C(13)	0·4570 (6)	−0·1751 (4)	0·4463 (1)	5·48 (8)
C(14)	0·6639 (6)	−0·0856 (4)	0·4396 (1)	5·25 (8)
C(15)	0·7500 (5)	−0·0430 (4)	0·3931 (1)	4·31 (7)
O(4)	−0·2557 (3)	0·4478 (2)	0·96926 (7)	5·21 (5)
O(5)	0·1223 (3)	0·3485 (2)	0·96356 (6)	4·89 (5)
O(6)	−0·1035 (3)	0·4422 (2)	0·71844 (6)	4·36 (5)
C(16)	−0·0952 (5)	0·3488 (3)	0·95207 (9)	3·46 (6)
C(17)	−0·1706 (5)	0·2255 (4)	0·91598 (9)	4·06 (7)
C(18)	−0·1461 (4)	0·2886 (3)	0·86390 (9)	3·04 (6)
C(19)	−0·3138 (5)	0·2457 (3)	0·83103 (9)	3·68 (7)
C(20)	−0·2940 (5)	0·2969 (4)	0·78334 (9)	3·82 (7)
C(21)	−0·1042 (4)	0·3956 (3)	0·76660 (9)	3·14 (6)
C(22)	0·0668 (5)	0·4407 (3)	0·79841 (9)	3·58 (7)
C(23)	0·0441 (5)	0·3851 (3)	0·84638 (9)	3·62 (7)
C(24)	0·0818 (5)	0·5510 (4)	0·6995 (1)	4·06 (7)
C(25)	0·0285 (5)	0·5929 (3)	0·64798 (9)	3·35 (6)
C(26)	−0·1756 (5)	0·6828 (4)	0·6371 (1)	4·50 (7)
C(27)	−0·2236 (5)	0·7229 (4)	0·5900 (1)	5·19 (8)
C(28)	−0·0636 (6)	0·6720 (4)	0·5527 (1)	5·38 (8)
C(29)	0·1408 (6)	0·5828 (4)	0·5627 (1)	5·20 (8)
C(30)	0·1861 (5)	0·5440 (4)	0·6102 (1)	4·40 (7)

Table 2. *Bond distances* (Å) *and angles* (°)

C(1)–O(1)	1·237 (2)	C(16)–O(4)	1·258 (2)
C(1)–O(2)	1·273 (2)	C(16)–O(5)	1·252 (2)
C(1)–C(2)	1·502 (3)	C(16)–C(17)	1·499 (3)
C(2)–C(3)	1·508 (3)	C(17)–C(18)	1·509 (3)
C(3)–C(4)	1·383 (3)	C(18)–C(19)	1·378 (3)
C(3)–C(8)	1·372 (3)	C(18)–C(23)	1·375 (3)
C(4)–C(5)	1·366 (3)	C(19)–C(20)	1·365 (3)
C(5)–C(6)	1·376 (3)	C(20)–C(21)	1·378 (3)
C(6)–C(7)	1·367 (3)	C(21)–C(22)	1·376 (3)
C(7)–C(8)	1·375 (3)	C(22)–C(23)	1·383 (3)
C(6)–O(3)	1·372 (2)	C(21)–O(6)	1·368 (2)
O(3)–C(9)	1·422 (2)	O(6)–C(24)	1·428 (3)
C(9)–C(10)	1·494 (3)	C(24)–C(25)	1·492 (3)
C(10)–C(11)	1·367 (3)	C(25)–C(26)	1·371 (3)
C(10)–C(15)	1·381 (3)	C(25)–C(30)	1·370 (3)
C(11)–C(12)	1·381 (3)	C(26)–C(27)	1·367 (3)
C(12)–C(13)	1·363 (4)	C(27)–C(28)	1·371 (3)
C(13)–C(14)	1·361 (4)	C(28)–C(29)	1·364 (3)
C(14)–C(15)	1·374 (3)	C(29)–C(30)	1·369 (3)
O(1)–H(O2)	1·52	O(4)–H(O4)	1·26
O(2)–H(O2)	1·21	O(5)–H(O4)	1·39
O(1)–C(1)–O(2)	123·0 (2)	O(4)–C(16) O(5)	123·4 (2)
O(1)–C(1)–C(2)	120·0 (2)	O(4)–C(16)–C(17)	117·8 (2)
O(2)–C(1)–C(2)	117·0 (2)	O(5)–C(16)–C(17)	118·9 (2)
C(1)–C(2)–C(3)	111·9 (2)	C(16)–C(17)–C(18)	112·9 (2)
C(2)–C(3)–C(4)	121·2 (2)	C(17)–C(18)–C(19)	120·2 (2)
C(2)–C(3)–C(8)	121·5 (2)	C(17)–C(18)–C(23)	122·9 (2)
C(4)–C(3)–C(8)	117·3 (2)	C(19)–C(18)–C(23)	116·9 (2)
C(3)–C(4)–C(5)	120·9 (2)	C(18)–C(19)–C(20)	121·8 (2)
C(4)–C(5)–C(6)	120·7 (2)	C(19)–C(20)–C(21)	120·5 (2)
C(5)–C(6)–C(7)	119·4 (2)	C(20)–C(21)–C(22)	119·3 (2)
C(5)–C(6)–O(3)	115·7 (2)	C(20)–C(21)–O(6)	115·8 (2)
C(7)–C(6)–O(3)	124·9 (2)	C(22)–C(21)–O(6)	125·0 (2)
C(6)–C(7)–C(8)	119·3 (2)	C(21)–C(22)–C(23)	119·1 (2)
C(7)–C(8)–C(3)	122·4 (2)	C(22)–C(23)–C(18)	122·5 (2)
C(6)–O(3)–C(9)	118·2 (2)	C(21)–O(6)–C(24)	118·4 (2)
O(3)–C(9)–C(10)	108·3 (2)	O(6)–C(24)–C(25)	107·5 (2)
C(9)–C(10)–C(11)	121·1 (2)	C(24)–C(25)–C(25)	121·4 (2)
C(9)–C(10)–C(15)	120·2 (2)	C(24)–C(25)–C(30)	120·4 (2)
C(11)–C(10)–C(15)	118·7 (2)	C(26)–C(25)–C(30)	118·2 (2)
C(10)–C(11)–C(12)	120·5 (2)	C(25)–C(26)–C(27)	121·5 (2)
C(11)–C(12)–C(13)	120·0 (3)	C(26)–C(27)–C(28)	119·2 (3)
C(12)–C(13)–C(14)	120·3 (3)	C(27)–C(28)–C(29)	120·2 (3)
C(13)–C(14)–C(15)	119·8 (3)	C(28)–C(29)–C(30)	119·8 (3)
C(14)–C(15)–C(10)	120·7 (3)	C(29)–C(30)–C(25)	121·1 (2)
O(1)–H(O2)–O(2)	164	O(4)–H(O4)–O(5)	169

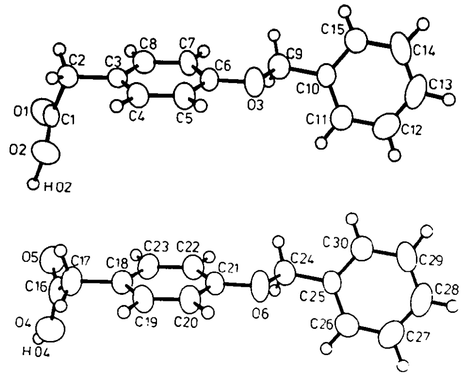

Fig. 1. Perspective views of the geometries of the two independent molecules.

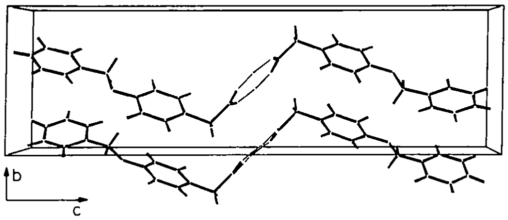

Fig. 2. View along **a*** of the molecular packing.

Table 3. *Relevant torsion angles* (*e.s.d.'s* 0·3°)

O(1)–C(1)–C(2)–C(3)	−98·4	O(4)–C(16)–C(17)–C(18)	89·2
O(2)–C(1)–C(2)–C(3)	80·8	O(5)–C(16)–C(17)–C(18)	−90·7
C(1)–C(2)–C(3)–C(4)	−95·6	C(16)–C(17)–C(18)–C(19)	−144·1
C(1)–C(2)–C(3)–C(8)	85·8	C(16)–C(17)–C(18)–C(23)	38·2
C(9)–O(3)–C(6)–C(7)	−0·2	C(24)–O(6)–C(21)–C(22)	−2·6
C(9)–O(3)–C(6)–C(5)	180·0	C(24)–O(6)–C(21)–C(20)	177·0
C(6)–O(3)–C(9)–C(10)	−176·1	C(21)–O(6)–C(24)–C(25)	−175·3
O(3)–C(9)–C(10)–C(11)	63·7	O(6)–C(24)–C(25)–C(26)	66·2
O(3)–C(9)–C(10)–C(15)	−118·3	O(6)–C(24)–C(25)–C(30)	−114·9

The geometries of the two independent molecules are similar except for the relative positions of the carboxyl groups. The carboxyl group forms a dihedral angle of 111·0 (3)° with the nearest phenyl group in molecule (I) and 104·0 (3)° in molecule (II). Though this non-planarity is required to avoid steric hindrance, the torsion angles leading to this arrangement are very different in the two molecules.

The dihedral angle between the two phenyl groups is 64·0 (3)° in (I) and 64·1 (3)° in (II) and results mainly from rotations about the C(9)–C(10) and C(24)–C(25) bonds, respectively. In this way a *gauche* conformation is obtained for the O(3)–C(9)–C(10)–C(11) and O(6)–C(24)–C(25)–C(26) angles which avoids steric hindrance of the O atom and the phenyl group. A similar effect is observed in a related compound in the following paper (Bats & Canenbley, 1984).

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[4-(Phenoxymethyl)phenyl]acetic Acid, $C_{15}H_{14}O_3$

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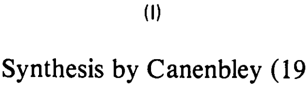
Abstract. $M_r = 242{\cdot}28$, monoclinic, $P2_1/a$, $a = 6{\cdot}901\,(1)$, $b = 6{\cdot}812\,(3)$, $c = 26{\cdot}523\,(4)$ Å, $\beta = 92{\cdot}58\,(2)°$, $V = 1245{\cdot}6\,(6)$ Å^3, $Z = 4$, $D_x = 1{\cdot}292\,(1)$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0{\cdot}8$ cm^{-1}, $F(000) = 512$, $T = 293$ K. Final $R = 0{\cdot}047$ for 1385 independent observed reflections. The molecules form centrosymmetric dimers by hydrogen bonding between two neighboring carboxyl groups. The (phenoxymethyl)phenyl group has the Z conformation required to avoid steric hindrance by the phenyl groups. The dihedral angle between the phenyl groups is 71·1 (2)°, of the same magnitude as the value found in the (benzyloxy)phenyl isomer.

Introduction. The title compound (I) was prepared in view of a possible analgetic activity. Although the compound is closely related to its active isomer [4-(benzyloxy)phenyl]acetic acid (Bats & Canenbley, 1984), no antiphlogistic activity was found. A crystal-structure determination was undertaken to allow for a structural comparison with related compounds.



(I)

Experimental. Synthesis by Canenbley (1983), colorless transparent plates by recrystallization from toluene/ether, crystal used: 0·05 × 0·575 × 0·875 mm, cell constants from setting angles of 25 reflections with $4 < \theta \leq 12°$, CAD-4 diffractometer, graphite monochromator, hemisphere up to $2\theta = 44°$, $(\sin\theta/\lambda)_{\max} = 0{\cdot}53$ Å^{-1}, range of hkl: h 0→7, k 0→7, l ±27, ω-scan, total number of reflections 3394, independent reflections 1514; three standard reflections every 4500 seconds remained stable; no absorption correction, averaging of equivalent reflections, $R_{\rm int} = 0{\cdot}030$, 1385 reflections with $I > 0{\cdot}3\sigma(I)$ used, weighting scheme $w(I) = 1/[\sigma^2(I) + (0{\cdot}03I)^2]$, structure determination by *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), all H-atom positions from difference synthesis and included in refinement but their isotropic thermal parameters fixed, refinement on F, extinction coefficient included, $(\Delta/\sigma)_{\max} = 0{\cdot}2$, final difference Fourier map peaks $< 0{\cdot}15$ e Å^{-3}, final $R = 0{\cdot}047$, $wR = 0{\cdot}042$, $S = 1{\cdot}54$, scattering factors from *International Tables for X-ray Crystallography* (1974), calculations with *SDP* program system (Enraf–Nonius, 1982).

Discussion. The positional parameters are reported in Table 1,* the bond lengths and angles in Table 2. Fig. 1 shows the molecular geometry and numbering scheme.

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