

## 2-Hydroxy-4,6-dimethoxy-3-(3-methylbutanoyl)benzaldehyde

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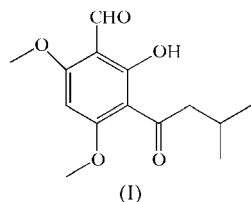
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The structure of the title compound, C<sub>14</sub>H<sub>18</sub>O<sub>5</sub>, has two independent molecules related by a local noncrystallographic *a*-glide plane perpendicular to the *b* axis. The pseudo-glide plane shows a discontinuity at *z* = 0. Both molecules have an intramolecular hydrogen bond between the hydroxy and aldehyde groups. There are stacks of molecules along the *a*-axis direction. Neighboring molecules in the stack have an interplanar angle of 1.6 (1)°, interplanar distances ranging between 3.399 (3) and 3.417 (3) Å, and a ring offset of 1.38 (1) Å.

## Comment

The title compound, (I), was obtained by a Friedel–Crafts acylation reaction of 4,6-dimethoxysalicylaldehyde with 3-methylbutyric acid chloride (Reggelin *et al.*, 1999). Only one of two possible regioisomers was obtained. The constitution of (I) could not be determined by HMBC correlations (Bax & Summers, 1986). Only after the application of 1,*n*-ADEQUATE experiments (Reif *et al.*, 1996) was it possible to ascertain the substitution pattern (Köck *et al.*, 1996). To corroborate the results from the NMR studies, a crystal structure analysis of (I) was performed.



The structure contains two independent molecules (*A* and *B*; Fig. 1). The dimensions of the two molecules are very similar; the r.m.s. deviation of a least-squares fit of the non-H atoms is 0.011 Å. In each of the molecules, there is an intramolecular O–H···O hydrogen bond between the hydroxy

group and the aldehyde group (Table 1). The aldehyde and the two methoxy groups are almost coplanar with the benzene plane. The angle between the plane of the benzene ring and the plane of the keto group attached to atom C1 (or C15) is 43.6 (1)° for both molecules. This nonplanar orientation is required to avoid a short repulsive contact between atoms O1 and O2 (or between O6 and O7).

The crystal structure shows stacks of molecules along the crystallographic *a*-axis direction. The order of the molecules in the stack is *ABAB*, *etc.*, as shown in Fig. 2. The interplanar angle between the benzene rings of molecules *A* and *B* is 1.6 (1)°. The perpendicular distance between the planes, defined as the shortest distance of a ring centroid from the plane of the adjacent ring, ranges from 3.399 (3) to 3.417 (3) Å. There is an offset of 1.38 (1) Å between the centroids of neighboring rings. There are intermolecular  $\pi$ – $\pi$  contacts between neighboring benzaldehyde groups. The shortest intermolecular C <sub>$\pi$</sub> ···C <sub>$\pi$</sub>  distances are between 3.335 (3) and 3.428 (3) Å and are illustrated in Fig. 2 as dotted lines. Those involving the aldehyde C atoms are slightly shorter than the perpendicular distances between the benzene planes. The molecules in the stack are also connected by four intermolecular C–H···O interactions (Table 1, entries 3 to 6), with H···O distances between 2.52 and 2.57 Å (also shown in

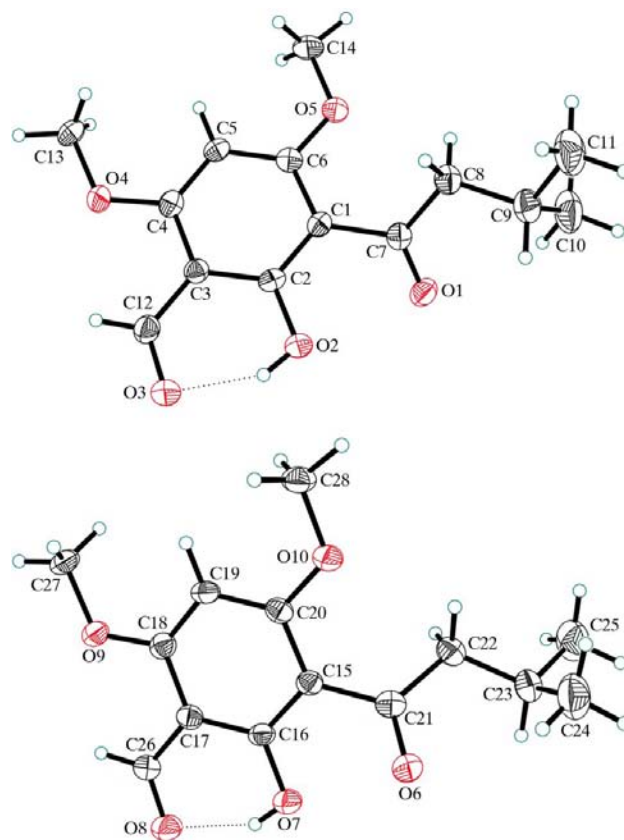
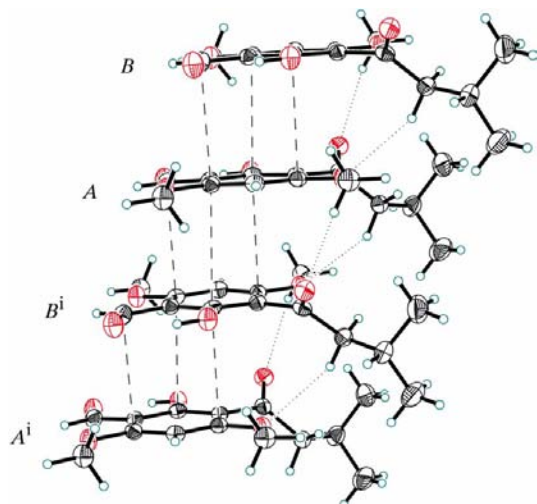


Figure 1

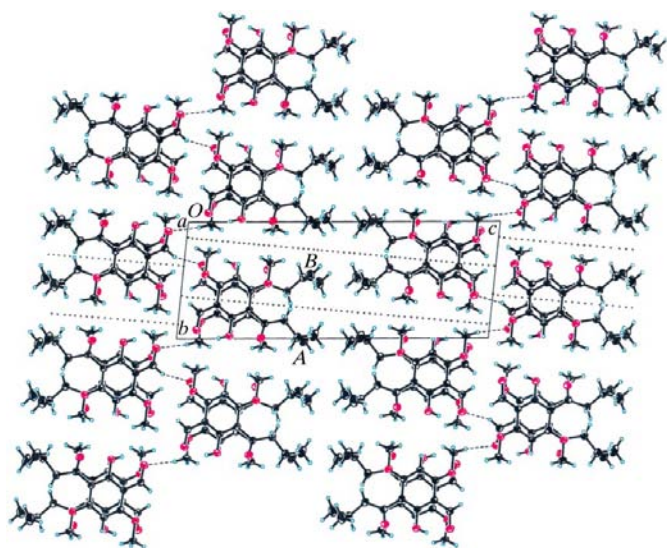
The two independent molecules, *A* (top) and *B* (bottom), of (I), with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are drawn as small spheres of arbitrary radii.

Fig. 2). The stacks are connected by additional intermolecular C—H···O contacts (Table 1, entries 7 and 8), with H···O distances of 2.47 and 2.52 Å, to bilayers parallel to the [001] plane, as shown in Fig. 3. There are also four intermolecular O<sub>keto</sub>···C<sub>methoxy</sub> interactions, with O···C distances of 2.910 (2), 2.929 (2), 3.015 (2) and 3.019 (2) Å, which connect the stacks in the *b*-axis direction. These O···C distances are significantly shorter than the van der Waals contact distance of 3.22 Å (Bondi, 1964), and the C=O···C and O···C—O angles are almost linear. No significant interactions are observed between neighboring bilayers in the *c*-axis direction.



**Figure 2**

The stacking of the molecules of (I). The shortest intermolecular C<sub>π</sub>···C<sub>π</sub> interactions are shown as broken lines and dotted lines represent intermolecular C—H···O interactions. [Symmetry code: (i)  $x + 1, y, z$ .]



**Figure 3**

A projection of the crystal packing of (I) down *a*. Dashed lines represent C—H···O interactions between stacks. The local pseudo-*a*-glide planes are shown as dotted lines. *A* and *B* represent the positions of molecules *A* and *B*.

The two molecules are related by pseudosymmetry. Inspection of the fractional coordinates shows the two molecules to be related by the pseudo-relationship  $x_A = x_B + 0.500$ ,  $y_A = 1.257 - y_B + 0.539z_B$  and  $z_A = z_B$ . This is a local noncrystallographic *a*-glide plane perpendicular to the *b* axis, intersecting the *b* axis at positions  $y = 0.128$  and  $y = 0.628$ , as shown in Fig. 3. The pseudo-glide plane is continuous in the crystallographic *a*-axis direction, resulting in a value of the unit-cell angle  $\gamma$  of approximately 90°. In the *c*-axis direction, the pseudo-glide plane acts only in one unit cell and shows discontinuities at  $z = 0$  and  $z = 1$ . Similar pseudosymmetry has been observed by us in other crystal structures (Bats, Hoyer & Mulzer, 1999; Bats, Öhlinger & Mulzer, 1999).

## Experimental

The preparation of (I) has been reported by Köck *et al.* (1996). Single crystals were obtained by slow evaporation of a solution of (I) in CDCl<sub>3</sub> at about 280 K.

### Crystal data

C <sub>14</sub> H <sub>18</sub> O <sub>5</sub>	$\gamma = 90.099 (6)^\circ$
$M_r = 266.28$	$V = 1326.9 (3) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 4$
$a = 7.2946 (10) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 8.2775 (13) \text{ \AA}$	$\mu = 0.10 \text{ mm}^{-1}$
$c = 22.400 (3) \text{ \AA}$	$T = 160 (2) \text{ K}$
$\alpha = 95.949 (6)^\circ$	$0.50 \times 0.22 \times 0.16 \text{ mm}$
$\beta = 99.410 (8)^\circ$	

### Data collection

Siemens SMART 1K CCD diffractometer	5830 independent reflections
19412 measured reflections	3128 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.067$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.051$	353 parameters
$wR(F^2) = 0.131$	H-atom parameters constrained
$S = 0.97$	$\Delta\rho_{\text{max}} = 0.23 \text{ e \AA}^{-3}$
5830 reflections	$\Delta\rho_{\text{min}} = -0.24 \text{ e \AA}^{-3}$

**Table 1**

Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2···O3	0.84	1.79	2.549 (2)	149
O7—H7···O8	0.84	1.80	2.558 (2)	149
C8—H8A···O10 <sup>i</sup>	0.99	2.57	3.372 (3)	139
C14—H14C···O6 <sup>i</sup>	0.98	2.52	3.277 (3)	134
C22—H22B···O5	0.99	2.57	3.371 (3)	138
C28—H28A···O1	0.98	2.52	3.277 (3)	134
C12—H12···O8 <sup>ii</sup>	0.95	2.47	3.337 (3)	152
C27—H27B···O3 <sup>iii</sup>	0.98	2.52	3.492 (3)	170

Symmetry codes: (i)  $x + 1, y, z$ ; (ii)  $-x + 1, -y + 1, -z$ ; (iii)  $-x + 1, -y + 2, -z$ .

H atoms were positioned geometrically and treated as riding [ $C_{\text{sp}^2}-\text{H} = 0.95 \text{ \AA}$ , primary C—H = 1.00 Å, secondary C—H = 0.99 Å, methyl C—H = 0.98 Å and O—H = 0.84 Å, and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  or  $1.5U_{\text{eq}}(\text{methyl C and O})$ ]. The torsion angle about the C—C axis was refined for the methyl groups and the torsion angle about the C—O axis was refined for the hydroxy group. The triclinic unit cell can be transformed to a C-centered cell with a monoclinic shape. The Laue symmetry, however, showed the structure to be triclinic ( $R_{\text{int}} = 0.067$ ) rather than monoclinic ( $R_{\text{int}} = 0.56$ ). The present unit cell can be reduced by the transformation  $a_{\text{red}} = -a$ ,

$b_{\text{red}} = b$  and  $c_{\text{red}} = -a - c$ . The choice of the reduced cell was found to depend on the exact value of the cell angle  $\beta$  and changed during the final refinement of the unit-cell parameters. The original setting was retained in this work.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1996); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ3095). Services for accessing these data are described at the back of the journal.

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