organic compounds

Methyl 6-acetyl-1,4-benzodioxine-2-carboxylate

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The title compound, $C_{12}H_{10}O_5$, was prepared as part of our study on obtaining pure regioselective Friedel–Crafts acetylation products. The molecule is planar with no hydrogen bonds found in the crystal structure. The molecules are stacked together through π–π interactions (centroid–centroid distance = 3.655 Å), with the stacks of molecules forming a zigzag packing arrangement stabilized by van der Waals forces.

Related literature

For regioselective Friedel–Crafts acetylation reactions, see: Mata & Suárez (1997); Thiéry et al. (1995). For related structures, see: Leger et al. (1983).
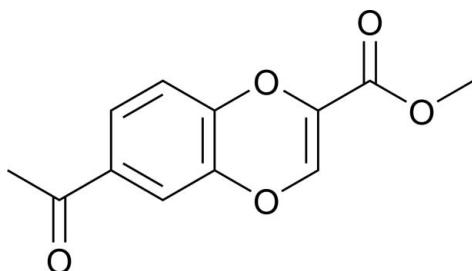
Experimental

Crystal data

$C_{12}H_{10}O_5$	V = 1053.6 (3) Å^3
M_r = 234.20	Z = 4
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
a = 7.2282 (11) Å	μ = 0.12 mm^{-1}
b = 25.147 (4) Å	T = 293 (2) K
c = 5.9639 (9) Å	0.52 × 0.23 × 0.18 mm
β = 103.598 (3)°	

Data collection

Bruker SMART CCD area-detector diffractometer	5915 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	2172 independent reflections
T_{min} = 0.757, T_{max} = 1.000	1409 reflections with $I > 2\sigma(I)$
(expected range = 0.741–0.979)	R_{int} = 0.079

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.052	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2)$ = 0.132	
S = 0.92	$\Delta\rho_{max}$ = 0.22 e Å^{-3}
2172 reflections	$\Delta\rho_{min}$ = −0.21 e Å^{-3}
195 parameters	

Data collection: SMART (Bruker, 2000); cell refinement: SAINT (Bruker, 2000); data reduction: SAINT and SHELTXL (Bruker, 2000); program(s) used to solve structure: SHELXS97 (Sheldrick, 1990); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL and ORTEP-3 (Farrugia, 1997); software used to prepare material for publication: SHELXTL.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FL2173).

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supplementary materials

Methyl 6-acetyl-1,4-benzodioxine-2-carboxylate

Y. Ding and **G. Yao**

Comment

The title compound was first obtained as a mixture with 7-acetyl-l,4-benzodioxin-2-carboxylic acid methyl ester nisomer in a ratio of 85:15 with total yield of 85%-87% by Friedel-Crafts actylation (Mata & Suárez, 1997). In order to get pure regioselective acylation products, we tried to use $AlCl_3$—CS_2 as reagent (Thiéry *et al.*, 1995) in the reaction and did obtain a pure acetylation product. In order to determine the location of the acetyl group, an X-ray structure determination of the title compound (I) has been carried out and the results are presented here (Fig.1).

As seen from Fig. 1, the acetyl group was located on C2 of phenyl ring, which confirms the acetylation position is at C-6 of 1,4-benzodioxin-2-carboxylic acid methyl ester and the acetylation product is the title compound (I). The 1,4-dioxin plane defined by O1/O2/C5/C6/C7/C8 and the phenyl ring defined by C1/C2/C3/C4/C5/C6 are coplanar with each other with a dihedral angle between their mean planes of 0.65 (0.06)°. These groups are also planar with the acetyl group and the ester group, forming torsion angles of C1—C2—C11—O5 [−3.2 (3)°] and C3—C2—C11—C12 [−4.2 (3)°], C7—C8—C9—O4 [9.3 (3)°] and O1—C8—C9—O3 [8.7 (2)°], respectively. Three other structures contining the 1,4-Benzodioxin-2-yl moiety have been published (Leger *et al.*, 1983).

No suitable hydrogen bonds are found in the crystal structure. In the crystal cell packing diagram (Fig. 2), the molecules are stacked together through $\pi \cdots \pi$ interactions, and stacks of molecules form a zigzag packing arrangement stabilized by van de Waals forces.

Experimental

The title compound was synthesized as described by Thiéry *et al.* (1995) from l,4-benzodioxin-2-carboxylic acid ethyl ester, acyl chloride and anhydrous $AlCl_3$ in CS_2(Fig. 3). The title compound was obtained as colorless needles, yields: 94%, mp 393 K. ^{1}H-NMR (CDC1$_3$): δ 2.50 (s, 3H, CH$_3$CO), 3.83 (s, 3H, OCH$_3$), 6.87 (d, J = 8.5 Hz, 1H, H-8), 6.98 (s, 1H, H-3), 7.31(d, J = 2.0 Hz, 1H, H-5), 7.53 (dd, J = 8.5, 2.0 Hz, 1H, H-7). Single crystals of (I) suitable for X-ray diffraction were obtained by slow evaporation of a MeOH-CHCl$_3$ solution.

Refinement

H atoms were refined with fixed individual displacement parameters [$U_{iso}(H) = 1.2U_{eq}(C)$ for CH and or $U_{iso}(H) = 1.5U_{eq}(C)$ for CH$_3$] using a riding model with C—H distances ranging from 0.93 to 1.01 Å.

supplementary materials

Figures
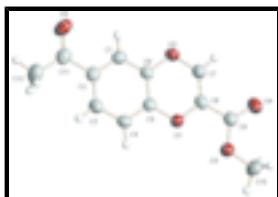
Fig. 1. The molecular structure of (I), showing the atom-labelling scheme and 50% probability displacement ellipsoids.
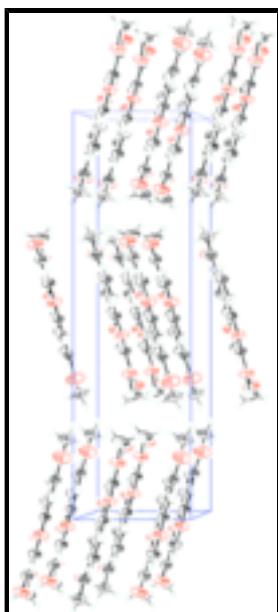
Fig. 2. The packing view of the title compound (I) along c axis.

Fig. 3. The reaction scheme.

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Crystal data

$C_{12}H_{10}O_5$	$D_x = 1.476$ Mg m^{-3}
$M_r = 234.20$	Melting point: 393 K
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 7.2282$ (11) Å	Cell parameters from 1401 reflections
$b = 25.147$ (4) Å	$\theta = 5.8–49.6°$
$c = 5.9639$ (9) Å	$\mu = 0.12$ mm^{-1}
$\beta = 103.598$ (3)°	$T = 293$ (2) K
$V = 1053.6$ (3) Å^3	Block, colorless
$Z = 4$	$0.52 \times 0.23 \times 0.18$ mm
$F_{000} = 488$	

Data collection

Bruker SMART CCD area-detector diffractometer	1409 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.079$
$T = 293(2)$ K	$\theta_{max} = 26.5°$
phi and ω scans	$\theta_{min} = 1.6°$
Absorption correction: Multi-scan (SADABS; Sheldrick, 1996)	$h = -9 \rightarrow 8$
$T_{min} = 0.757$, $T_{max} = 1.000$	$k = -31 \rightarrow 29$
5915 measured reflections	$l = -6 \rightarrow 7$
2172 independent reflections	

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.052$	$w = 1/[\sigma^2(F_o{}^2) + (0.0666P)^2]$ where $P = (F_o{}^2 + 2F_c{}^2)/3$
$wR(F^2) = 0.132$	$(\Delta/\sigma)_{max} = 0.006$
$S = 0.92$	$\Delta\rho_{max} = 0.22$ e Å^{-3}
2172 reflections	$\Delta\rho_{min} = -0.20$ e Å^{-3}
195 parameters	Extinction correction: SHELXL97, $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.017 (3)
Secondary atom site location: difference Fourier map	

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Least-squares planes (*x,y,z* in crystal coordinates) and deviations from them (* indicates atom used to define plane)

6.9022 (0.0019) *x* + 6.9493 (0.0175) *y* − 1.9684 (0.0042) *z* = 4.2331 (0.0098)

* 0.0008 (0.0013) C1 * 0.0003 (0.0013) C2 * −0.0033 (0.0013) C3 * 0.0053 (0.0013) C4 * −0.0042 (0.0013) C5 * 0.0012 (0.0013) C6

Rms deviation of fitted atoms = 0.0031

6.9132 (0.0018) *x* + 6.9225 (0.0179) *y* − 1.9054 (0.0035) *z* = 4.2516 (0.0085)

Angle to previous plane (with approximate e.s.d.) = 0.65 (0.06)

* −0.0012 (0.0011) O1 * 0.0013 (0.0011) O2 * 0.0052 (0.0012) C5 * −0.0052 (0.0012) C6 * 0.0027 (0.0013) C7 * −0.0028 (0.0012) C8

Rms deviation of fitted atoms = 0.0035

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$)

	x	y	z	$U_{iso}*/U_{eq}$
O1	0.35476 (17)	0.45094 (4)	0.69473 (18)	0.0474 (4)
O2	0.20608 (19)	0.46719 (5)	0.21300 (19)	0.0529 (4)
O3	0.4490 (2)	0.35620 (5)	0.8458 (2)	0.0554 (4)
O4	0.4360 (2)	0.32251 (5)	0.4951 (2)	0.0674 (5)
O5	0.0113 (3)	0.65702 (6)	0.1407 (3)	0.0841 (5)
C1	0.1371 (3)	0.55620 (7)	0.2935 (3)	0.0437 (5)
C2	0.1378 (2)	0.59835 (6)	0.4449 (3)	0.0427 (4)
C3	0.2126 (3)	0.58992 (7)	0.6794 (3)	0.0455 (5)
C4	0.2862 (3)	0.54074 (7)	0.7596 (3)	0.0441 (5)
C5	0.2828 (2)	0.49959 (6)	0.6071 (3)	0.0383 (4)
C6	0.2086 (2)	0.50773 (6)	0.3728 (3)	0.0391 (4)
C7	0.2794 (3)	0.41997 (7)	0.3069 (3)	0.0468 (5)
C8	0.3480 (2)	0.41189 (6)	0.5290 (3)	0.0410 (4)
C9	0.4162 (3)	0.35916 (7)	0.6169 (3)	0.0449 (5)
C10	0.4945 (5)	0.30349 (9)	0.9420 (4)	0.0731 (8)
C11	0.0631 (3)	0.65106 (7)	0.3482 (3)	0.0519 (5)
C12	0.0555 (4)	0.69607 (9)	0.5089 (5)	0.0681 (7)
H1	0.083 (2)	0.5606 (7)	0.130 (3)	0.056 (5)*
H2	0.217 (3)	0.6176 (8)	0.786 (3)	0.057 (6)*
H3	0.338 (2)	0.5343 (7)	0.927 (3)	0.059 (6)*
H4	0.266 (3)	0.3939 (9)	0.186 (3)	0.067 (6)*
H5	0.501 (3)	0.3071 (11)	1.113 (5)	0.109 (9)*
H6	0.620 (3)	0.2945 (10)	0.922 (4)	0.101 (10)*
H7	0.395 (4)	0.2768 (11)	0.869 (4)	0.112 (10)*
H8	−0.016 (3)	0.7269 (10)	0.427 (4)	0.097 (8)*
H9	0.182 (4)	0.7100 (12)	0.592 (5)	0.106 (11)*
H10	−0.016 (3)	0.6863 (10)	0.625 (5)	0.104 (10)*

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0722 (9)	0.0322 (6)	0.0347 (7)	0.0072 (6)	0.0066 (6)	−0.0009 (5)
O2	0.0824 (10)	0.0409 (7)	0.0313 (7)	0.0105 (6)	0.0049 (6)	−0.0036 (5)
O3	0.0904 (11)	0.0350 (7)	0.0398 (8)	0.0104 (6)	0.0133 (7)	0.0029 (5)
O4	0.1143 (13)	0.0404 (8)	0.0489 (8)	0.0128 (7)	0.0223 (8)	−0.0059 (6)

O5	0.1253 (14)	0.0571 (10)	0.0602 (10)	0.0223 (9)	0.0023 (9)	0.0156 (8)
C1	0.0509 (11)	0.0436 (10)	0.0352 (10)	0.0012 (8)	0.0075 (8)	0.0040 (8)
C2	0.0477 (11)	0.0356 (9)	0.0460 (10)	−0.0016 (8)	0.0134 (8)	0.0029 (8)
C3	0.0625 (12)	0.0351 (10)	0.0388 (10)	−0.0015 (8)	0.0121 (9)	−0.0046 (8)
C4	0.0595 (12)	0.0395 (10)	0.0330 (9)	0.0001 (8)	0.0105 (8)	−0.0009 (8)
C5	0.0453 (11)	0.0334 (9)	0.0365 (9)	−0.0001 (7)	0.0102 (7)	0.0025 (7)
C6	0.0474 (11)	0.0350 (9)	0.0356 (9)	−0.0014 (7)	0.0109 (8)	−0.0020 (7)
C7	0.0658 (13)	0.0363 (9)	0.0373 (10)	0.0038 (9)	0.0102 (9)	−0.0040 (8)
C8	0.0527 (11)	0.0343 (9)	0.0375 (10)	−0.0015 (8)	0.0134 (8)	−0.0045 (7)
C9	0.0569 (12)	0.0373 (10)	0.0413 (10)	0.0007 (8)	0.0131 (9)	−0.0017 (8)
C10	0.123 (3)	0.0399 (12)	0.0553 (15)	0.0178 (14)	0.0183 (15)	0.0128 (10)
C11	0.0561 (13)	0.0414 (10)	0.0565 (13)	0.0015 (9)	0.0095 (10)	0.0057 (9)
C12	0.0884 (19)	0.0361 (11)	0.0763 (17)	0.0080 (11)	0.0126 (15)	0.0008 (11)

Geometric parameters (Å, °)

O1—C5	1.3829 (19)	C3—H2	0.938 (19)
O1—C8	1.3858 (19)	C4—C5	1.374 (2)
O2—C7	1.366 (2)	C4—H3	0.993 (17)
O2—C6	1.3927 (19)	C5—C6	1.389 (2)
O3—C9	1.332 (2)	C7—C8	1.317 (2)
O3—C10	1.451 (2)	C7—H4	0.96 (2)
O4—C9	1.203 (2)	C8—C9	1.468 (2)
O5—C11	1.215 (2)	C10—H5	1.01 (3)
C1—C6	1.364 (2)	C10—H6	0.97 (2)
C1—C2	1.392 (2)	C10—H7	1.00 (3)
C1—H1	0.965 (17)	C11—C12	1.492 (3)
C2—C3	1.392 (2)	C12—H8	0.99 (2)
C2—C11	1.495 (2)	C12—H9	0.99 (3)
C3—C4	1.386 (2)	C12—H10	0.99 (3)
C5—O1—C8	114.21 (12)	O2—C7—H4	109.0 (12)
C7—O2—C6	114.49 (13)	C7—C8—O1	123.37 (15)
C9—O3—C10	115.18 (16)	C7—C8—C9	120.94 (16)
C6—C1—C2	120.80 (16)	O1—C8—C9	115.65 (14)
C6—C1—H1	118.8 (11)	O4—C9—O3	123.97 (16)
C2—C1—H1	120.4 (11)	O4—C9—C8	123.65 (17)
C1—C2—C3	118.50 (16)	O3—C9—C8	112.36 (15)
C1—C2—C11	118.65 (16)	O3—C10—H5	105.6 (15)
C3—C2—C11	122.83 (16)	O3—C10—H6	107.2 (15)
C4—C3—C2	120.62 (16)	H5—C10—H6	109 (2)
C4—C3—H2	118.7 (11)	O3—C10—H7	111.5 (16)
C2—C3—H2	120.7 (11)	H5—C10—H7	111 (2)
C5—C4—C3	119.85 (16)	H6—C10—H7	113 (2)
C5—C4—H3	119.1 (10)	O5—C11—C12	120.76 (18)
C3—C4—H3	121.1 (10)	O5—C11—C2	119.93 (18)
C4—C5—O1	117.99 (15)	C12—C11—C2	119.31 (18)
C4—C5—C6	119.83 (16)	C11—C12—H8	111.6 (14)
O1—C5—C6	122.18 (15)	C11—C12—H9	114.7 (17)
C1—C6—C5	120.38 (16)	H8—C12—H9	106 (2)

C1—C6—O2	118.26 (15)	C11—C12—H10	111.5 (15)
C5—C6—O2	121.36 (15)	H8—C12—H10	104 (2)
C8—C7—O2	124.38 (16)	H9—C12—H10	108 (2)
C8—C7—H4	126.5 (12)		
C6—C1—C2—C3	−0.2 (3)	C7—O2—C6—C5	0.7 (2)
C6—C1—C2—C11	178.17 (17)	C6—O2—C7—C8	0.1 (3)
C1—C2—C3—C4	0.6 (3)	O2—C7—C8—O1	−0.5 (3)
C11—C2—C3—C4	−177.70 (18)	O2—C7—C8—C9	177.14 (17)
C2—C3—C4—C5	−1.0 (3)	C5—O1—C8—C7	0.1 (3)
C3—C4—C5—O1	−178.92 (17)	C5—O1—C8—C9	−177.66 (15)
C3—C4—C5—C6	1.1 (3)	C10—O3—C9—O4	−5.6 (3)
C8—O1—C5—C4	−179.24 (15)	C10—O3—C9—C8	172.8 (2)
C8—O1—C5—C6	0.7 (2)	C7—C8—C9—O4	9.3 (3)
C2—C1—C6—C5	0.3 (3)	O1—C8—C9—O4	−172.86 (17)
C2—C1—C6—O2	−179.30 (16)	C7—C8—C9—O3	−169.07 (17)
C4—C5—C6—C1	−0.7 (3)	O1—C8—C9—O3	8.7 (2)
O1—C5—C6—C1	179.31 (15)	C1—C2—C11—O5	−3.2 (3)
C4—C5—C6—O2	178.80 (15)	C3—C2—C11—O5	175.04 (19)
O1—C5—C6—O2	−1.2 (3)	C1—C2—C11—C12	177.5 (2)
C7—O2—C6—C1	−179.73 (17)	C3—C2—C11—C12	−4.2 (3)

Fig. 1

Fig. 2

Fig. 3

(I)