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Ethyl 2-(3-acetyl-6-methyl-2-oxo-2*H*-pyran-4-yloxy)acetate

Muhammad Rabnawaz,[a] Stacy D. Benson,[b] Burhan Khan[a] and Muhammad Raza Shah[a]*

[a]H.E.J. Research Institute of Chemistry, International Center for Chemical and Biological Sciences, University of Karachi, Karachi 75270, Pakistan, and [b]Oklahoma State University, Department of Chemistry, 107 Physical Sciences, Stillwater, OK 74078-3071, USA
Correspondence e-mail: raza_shahm@yahoo.com

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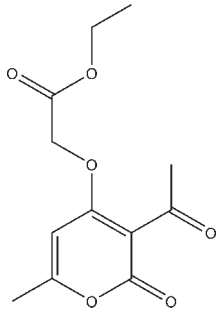
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.002 Å; R factor = 0.050; wR factor = 0.159; data-to-parameter ratio = 18.3.

The title compound, $C_{12}H_{14}O_6$, features a roughly planar molecule (r.m.s. deviation for all non-H atoms = 0.287 Å). In the crystal, the molecules are held together by C—H···O hydrogen bonds.

Related literature

For the use of dehydroacetic acid as a starting material in the synthesis of heterocyclic ring systems, see: Prakash *et al.* (2004), and of biologically important molecules such as coumarins, see: Hernandez-Galan *et al.* (1993).



Experimental

Crystal data

$C_{12}H_{14}O_6$ M_r = 254.23
Triclinic, $P\overline{1}$
a = 7.8258 (10) Å
b = 8.2722 (11) Å
c = 10.0838 (13) Å
α = 77.374 (7)°
β = 77.759 (6)°
γ = 88.857 (7)°
V = 622.28 (14) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.11 mm^{-1}
T = 298 K
0.72 × 0.13 × 0.11 mm

Data collection

Bruker SMART APEXII diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
T_{min} = 0.925, T_{max} = 0.988
14279 measured reflections
3039 independent reflections
2330 reflections with $I > 2\sigma(I)$
R_{int} = 0.036

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.050
$wR(F^2)$ = 0.159
S = 1.04
3039 reflections
166 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.35 e Å^{-3}
$\Delta\rho_{min}$ = −0.20 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C6A—H6A1···O2^{i}	0.96	2.53	3.462 (2)	165
C5—H5···O3A^{i}	0.93	2.38	3.3053 (19)	174
C2A—H2A1···O3A^{i}	0.97	2.57	3.355 (2)	138
C2E—H2E2···O1^{ii}	0.96	2.54	3.484 (3)	169

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

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT-Plus* (Bruker, 2008); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT5170).

References

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Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supporting information

Acta Cryst. (2010). E**66**, o397 [https://doi.org/10.1107/S1600536810001601]

Ethyl 2-(3-acetyl-6-methyl-2-oxo-2*H*-pyran-4-yloxy)acetate

Muhammad Rabnawaz, Stacy D. Benson, Burhan Khan and Muhammad Raza Shah

S1. Comment

3-Acetyl-4-hydroxy-6-methyl-2-oxo-2*H*-pyran (dehydroacetic acid) is a versatile starting material for the synthesis of a wide variety of heterocyclic ring systems (Prakash *et al.*, 2004) and biologically important molecules like coumarins (Hernandez-Galan *et al.*, 1993).

S2. Experimental

The dehydroacetic acid (500 mg, 3 mmol) was treated with ethylbromoacetate (2 g, 12 mmol) in acetone in the presence of K_2CO_3 (1.6 g, 12 mmol). The reaction mixture was refluxed for 3 h monitored with TLC at regular intervals of 30 minutes. The reaction was quenched by addition of 1 N HCl (10 ml) and the aqueous layer was extracted with ethyl acetate three times. The combined organic layers were concentrated under reduced pressure. The crude residue was dissolved in hot ethanol. The slow evaporation of ethanol yielded colorless needle-like crystals (90%, 680 mg).

S3. Refinement

The H atoms were placed in calculated positions and allowed to ride on their carrier atoms with C—H = 0.93–0.96 Å and with $U_{iso} = 1.2U_{eq}$(C) for CH and CH_2 and $U_{iso} = 1.5U_{eq}$(C) for CH_3 groups.

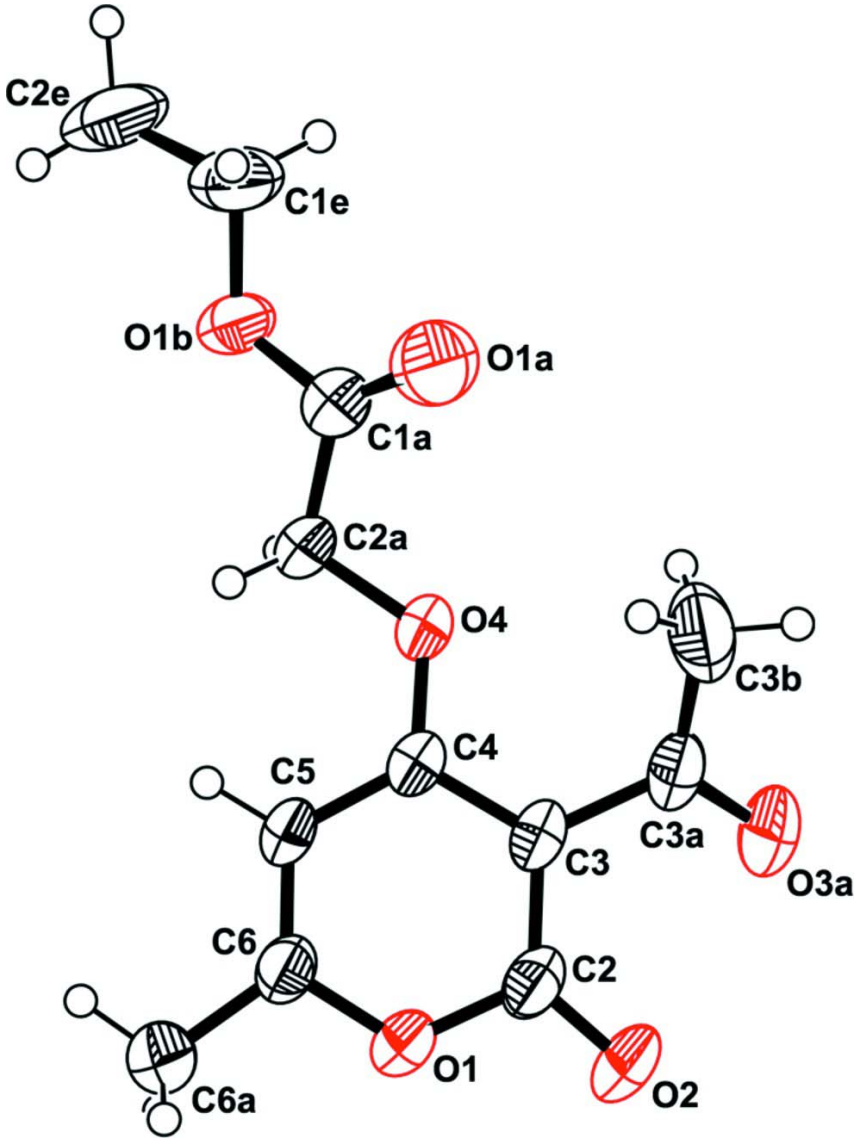

Figure 1

Crystal Structure of Ethyl 2-(3-acetyl-6-methyl-2-oxo-2*H*-pyran-4-yloxy) acetate (50% ellipsoids).

Ethyl 2-(3-acetyl-6-methyl-2-oxo-2*H*-pyran-4-yloxy)acetate

Crystal data

$C_{12}H_{14}O_6$
$M_r = 254.23$
Triclinic, $P\overline{1}$
Hall symbol: -P 1
$a = 7.8258\ (10)$ Å
$b = 8.2722\ (11)$ Å
$c = 10.0838\ (13)$ Å
$\alpha = 77.374\ (7)°$
$\beta = 77.759\ (6)°$
$\gamma = 88.857\ (7)°$
$V = 622.28\ (14)$ Å^3
$Z = 2$
$F(000) = 268$
$D_x = 1.357$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 6664 reflections
$\theta = 2.1–28.3°$
$\mu = 0.11$ mm^{-1}
$T = 298$ K
Rectangular prism, clear colourless
0.72 × 0.13 × 0.11 mm

Data collection

Bruker SMART APEXII diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 83.33 pixels mm^{-1}
φ scans and ω scans with κ offsets
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
T_{min} = 0.925, T_{max} = 0.988

14279 measured reflections
3039 independent reflections
2330 reflections with $I > 2\sigma(I)$
R_{int} = 0.036
θ_{max} = 28.3°, θ_{min} = 2.1°
h = −10→10
k = −11→10
l = −13→13

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.050
$wR(F^2)$ = 0.159
S = 1.04
3039 reflections
166 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0773P)^2 + 0.1512P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.35 e Å^{-3}
$\Delta\rho_{min}$ = −0.20 e Å^{-3}

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.

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 $F^2 > 2\sigma(F^2)$ 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	0.57091 (13)	0.60585 (14)	1.11130 (11)	0.0528 (3)
C2	0.44227 (18)	0.6846 (2)	1.04378 (17)	0.0494 (4)
C3	0.50118 (17)	0.81700 (18)	0.92489 (15)	0.0438 (3)
C4	0.67613 (17)	0.86621 (18)	0.89085 (15)	0.0419 (3)
C5	0.79728 (17)	0.78287 (18)	0.96663 (16)	0.0445 (3)
H5	0.9142	0.8175	0.9433	0.053*
C6	0.74139 (18)	0.65385 (19)	1.07210 (15)	0.0453 (3)
C6A	0.8505 (2)	0.5494 (2)	1.15859 (19)	0.0626 (5)
H6A1	0.9708	0.5851	1.1248	0.094*
H6A2	0.8379	0.4358	1.1537	0.094*
H6A3	0.8134	0.5597	1.2534	0.094*
C3A	0.36798 (19)	0.8935 (2)	0.84701 (18)	0.0525 (4)
C3B	0.4174 (3)	0.9705 (5)	0.6972 (3)	0.1171 (12)
H3B1	0.3199	0.9630	0.6548	0.176*
H3B2	0.5145	0.9138	0.6542	0.176*
H3B3	0.4499	1.0849	0.6854	0.176*

O3A	0.21609 (15)	0.8898 (2)	0.90547 (17)	0.0803 (5)
O4	0.72493 (13)	0.99457 (14)	0.78399 (13)	0.0576 (3)
C1A	0.9346 (2)	1.1577 (2)	0.60243 (17)	0.0525 (4)
C2A	0.8981 (2)	1.0641 (2)	0.74992 (18)	0.0562 (4)
H2A1	0.9816	0.9768	0.7622	0.067*
H2A2	0.9088	1.1378	0.8106	0.067*
O2	0.29702 (14)	0.62711 (18)	1.09368 (15)	0.0704 (4)
O1A	0.8501 (2)	1.1503 (2)	0.51873 (16)	0.0947 (6)
O1B	1.08032 (15)	1.24797 (15)	0.57701 (11)	0.0587 (3)
C1E	1.1521 (3)	1.3319 (3)	0.43439 (19)	0.0748 (6)
H1E1	1.0694	1.4101	0.3996	0.090*
H1E2	1.1769	1.2523	0.3755	0.090*
C2E	1.3156 (3)	1.4200 (4)	0.4343 (3)	0.1057 (9)
H2E1	1.2882	1.5037	0.4875	0.159*
H2E2	1.3712	1.4710	0.3404	0.159*
H2E3	1.3930	1.3424	0.4747	0.159*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0358 (5)	0.0632 (7)	0.0518 (6)	−0.0105 (5)	−0.0048 (4)	0.0003 (5)
C2	0.0325 (7)	0.0602 (9)	0.0533 (8)	−0.0079 (6)	−0.0035 (6)	−0.0126 (7)
C3	0.0282 (6)	0.0524 (8)	0.0514 (8)	−0.0040 (6)	−0.0069 (6)	−0.0141 (6)
C4	0.0306 (6)	0.0461 (7)	0.0475 (7)	−0.0052 (5)	−0.0062 (5)	−0.0084 (6)
C5	0.0280 (6)	0.0528 (8)	0.0512 (8)	−0.0071 (5)	−0.0080 (5)	−0.0077 (6)
C6	0.0338 (7)	0.0543 (8)	0.0469 (7)	−0.0054 (6)	−0.0076 (6)	−0.0096 (6)
C6A	0.0500 (9)	0.0741 (11)	0.0578 (10)	−0.0051 (8)	−0.0168 (7)	0.0039 (8)
C3A	0.0312 (7)	0.0618 (9)	0.0665 (10)	−0.0022 (6)	−0.0129 (6)	−0.0156 (8)
C3B	0.0486 (11)	0.212 (3)	0.0718 (14)	0.0101 (15)	−0.0214 (10)	0.0165 (17)
O3A	0.0314 (6)	0.1083 (11)	0.0932 (10)	0.0034 (6)	−0.0130 (6)	−0.0053 (8)
O4	0.0332 (5)	0.0616 (7)	0.0687 (7)	−0.0110 (5)	−0.0157 (5)	0.0110 (5)
C1A	0.0461 (8)	0.0541 (9)	0.0544 (9)	−0.0057 (7)	−0.0108 (7)	−0.0052 (7)
C2A	0.0361 (7)	0.0655 (10)	0.0578 (9)	−0.0158 (7)	−0.0116 (6)	0.0090 (7)
O2	0.0346 (6)	0.0894 (9)	0.0752 (8)	−0.0196 (6)	−0.0017 (5)	−0.0007 (7)
O1A	0.0861 (11)	0.1290 (14)	0.0670 (9)	−0.0384 (10)	−0.0321 (8)	0.0022 (9)
O1B	0.0544 (7)	0.0653 (7)	0.0469 (6)	−0.0197 (5)	−0.0051 (5)	0.0040 (5)
C1E	0.0799 (13)	0.0853 (13)	0.0456 (9)	−0.0179 (10)	−0.0010 (9)	0.0044 (9)
C2E	0.0910 (17)	0.127 (2)	0.0702 (13)	−0.0493 (15)	0.0077 (12)	0.0197 (13)

Geometric parameters (Å, º)

O1—C6	1.3501 (16)	C3B—H3B1	0.9600
O1—C2	1.404 (2)	C3B—H3B2	0.9600
C2—O2	1.2024 (17)	C3B—H3B3	0.9600
C2—C3	1.436 (2)	O4—C2A	1.4256 (17)
C3—C4	1.3856 (17)	C1A—O1A	1.189 (2)
C3—C3A	1.486 (2)	C1A—O1B	1.3228 (18)
C4—O4	1.3326 (18)	C1A—C2A	1.489 (2)

C4—C5	1.417 (2)	C2A—H2A1	0.9700
C5—C6	1.337 (2)	C2A—H2A2	0.9700
C5—H5	0.9300	O1B—C1E	1.450 (2)
C6—C6A	1.481 (2)	C1E—C2E	1.485 (3)
C6A—H6A1	0.9600	C1E—H1E1	0.9700
C6A—H6A2	0.9600	C1E—H1E2	0.9700
C6A—H6A3	0.9600	C2E—H2E1	0.9600
C3A—O3A	1.2073 (19)	C2E—H2E2	0.9600
C3A—C3B	1.476 (3)	C2E—H2E3	0.9600

C6—O1—C2	122.89 (12)	H3B1—C3B—H3B2	109.5
O2—C2—O1	113.96 (15)	C3A—C3B—H3B3	109.5
O2—C2—C3	129.34 (16)	H3B1—C3B—H3B3	109.5
O1—C2—C3	116.68 (12)	H3B2—C3B—H3B3	109.5
C4—C3—C2	118.59 (13)	C4—O4—C2A	121.02 (12)
C4—C3—C3A	124.32 (14)	O1A—C1A—O1B	124.77 (16)
C2—C3—C3A	117.09 (12)	O1A—C1A—C2A	126.07 (16)
O4—C4—C3	117.09 (13)	O1B—C1A—C2A	109.14 (14)
O4—C4—C5	121.74 (12)	O4—C2A—C1A	108.53 (13)
C3—C4—C5	121.17 (13)	O4—C2A—H2A1	110.0
C6—C5—C4	119.19 (12)	C1A—C2A—H2A1	110.0
C6—C5—H5	120.4	O4—C2A—H2A2	110.0
C4—C5—H5	120.4	C1A—C2A—H2A2	110.0
C5—C6—O1	121.31 (13)	H2A1—C2A—H2A2	108.4
C5—C6—C6A	126.34 (14)	C1A—O1B—C1E	117.97 (14)
O1—C6—C6A	112.35 (13)	O1B—C1E—C2E	107.09 (17)
C6—C6A—H6A1	109.5	O1B—C1E—H1E1	110.3
C6—C6A—H6A2	109.5	C2E—C1E—H1E1	110.3
H6A1—C6A—H6A2	109.5	O1B—C1E—H1E2	110.3
C6—C6A—H6A3	109.5	C2E—C1E—H1E2	110.3
H6A1—C6A—H6A3	109.5	H1E1—C1E—H1E2	108.6
H6A2—C6A—H6A3	109.5	C1E—C2E—H2E1	109.5
O3A—C3A—C3B	118.99 (17)	C1E—C2E—H2E2	109.5
O3A—C3A—C3	119.99 (16)	H2E1—C2E—H2E2	109.5
C3B—C3A—C3	120.99 (14)	C1E—C2E—H2E3	109.5
C3A—C3B—H3B1	109.5	H2E1—C2E—H2E3	109.5
C3A—C3B—H3B2	109.5	H2E2—C2E—H2E3	109.5

C6—O1—C2—O2	−179.01 (14)	C2—O1—C6—C5	1.2 (2)
C6—O1—C2—C3	2.6 (2)	C2—O1—C6—C6A	−179.19 (14)
O2—C2—C3—C4	177.25 (16)	C4—C3—C3A—O3A	−153.29 (17)
O1—C2—C3—C4	−4.6 (2)	C2—C3—C3A—O3A	26.1 (2)
O2—C2—C3—C3A	−2.2 (3)	C4—C3—C3A—C3B	28.5 (3)
O1—C2—C3—C3A	175.96 (13)	C2—C3—C3A—C3B	−152.2 (2)
C2—C3—C4—O4	−176.87 (13)	C3—C4—O4—C2A	173.81 (14)
C3A—C3—C4—O4	2.5 (2)	C5—C4—O4—C2A	−6.3 (2)
C2—C3—C4—C5	3.3 (2)	C4—O4—C2A—C1A	159.18 (14)
C3A—C3—C4—C5	−177.39 (14)	O1A—C1A—C2A—O4	−13.5 (3)

O4—C4—C5—C6	−179.39 (14)	O1B—C1A—C2A—O4	168.37 (13)
C3—C4—C5—C6	0.5 (2)	O1A—C1A—O1B—C1E	−6.2 (3)
C4—C5—C6—O1	−2.8 (2)	C2A—C1A—O1B—C1E	172.01 (16)
C4—C5—C6—C6A	177.66 (16)	C1A—O1B—C1E—C2E	−178.72 (19)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C6*A*—H6*A*1···O2^{i}	0.96	2.53	3.462 (2)	165
C5—H5···O3*A*^{i}	0.93	2.38	3.3053 (19)	174
C2*A*—H2*A*1···O3*A*^{i}	0.97	2.57	3.355 (2)	138
C2*E*—H2*E*2···O1^{ii}	0.96	2.54	3.484 (3)	169

Symmetry codes: (i) *x*+1, *y*, *z*; (ii) *x*+1, *y*+1, *z*−1.