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3,5-Diacetylheptane-2,6-dione

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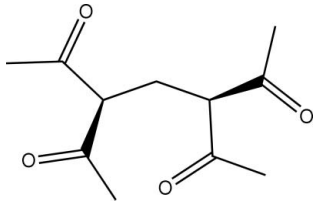
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.002 Å; R factor = 0.041; wR factor = 0.113; data-to-parameter ratio = 18.9.

The title compound, $C_{11}H_{16}O_4$, was produced when pentane-2,4-dione (acacH) was treated with formaldehyde in a *ca* 2.16:1 molar ratio. The compound exists in the solid state as the keto tautomer, although the enol tautomer also exists in solution. The C=O distances are in the range 1.2097 (18)–1.2169 (18) Å. Intermolecular C=O···C=O interactions exist, the shortest having a C···O distance of 3.378 (2) Å.

Related literature

The title compound was described over 100 years ago (Scholtz, 1897; Knoevenagel *et al.*, 1903). We have recently reported the structure of 1,1′,1″-[(5*R*,6*R*)-6-hydroxy-6-methyltetrahydro-2*H*-pyran-3,3,5-triyl]triethanone (Burton *et al.*, 2007), which is formed when excess formaldehyde is used in the synthesis. For related literature, see: Allen *et al.* (1998); Wilson (1963).



Experimental

Crystal data

$C_{11}H_{16}O_4$
M_r = 212.24
Orthorhombic, $P2_12_12_1$
a = 7.810 (2) Å
b = 8.611 (2) Å
c = 17.431 (4) Å
V = 1172.3 (5) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 100 K
0.47 × 0.43 × 0.40 mm

Data collection

Nonius KappaCCD diffractometer (with Oxford Cryostream)
Absorption correction: none
15692 measured reflections
2647 independent reflections
2352 reflections with $I > 2\sigma(I)$
R_{int} = 0.016

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.113
S = 1.04
2647 reflections
140 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.18 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C2	1.2145 (15)	C2—C3	1.5256 (17)
O2—C4	1.2097 (18)	C3—C4	1.5284 (17)
O3—C8	1.2169 (18)	C8—C9	1.5256 (18)
O4—C10	1.2158 (17)	C9—C10	1.5301 (17)
O1—C2—C3—C6	−15.71 (16)	O3—C8—C9—C6	−15.27 (16)
C6—C3—C4—O2	103.37 (14)	C6—C9—C10—O4	112.32 (14)

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); 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: BQ2022).

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supplementary materials

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3,5-Diacetylheptane-2,6-dione

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Comment

The title compound, (I), was first explored by Scholtz (1897) and Knoevenagel *et al.* (1903). Our goal was to utilize the title compound (I) in the preparation of polynuclear metal complexes.

Solutions of (I) in $CHCl_3$ show evidence in ^1H NMR spectra for both keto and enol tautomers, but the crystal contains only the keto form. C3 and C9 (Fig. 1) are protonated and tetrahedral, all the C—C bond lengths to them are typical of single bonds, and the four C═O distances (Table 1) are typical of double bonds.

Allen *et al.* (1998) have shown that intermolecular carbonyl···carbonyl interactions in ketones can significantly influence the packing of such molecules, and have identified three major geometric types. The shortest such contact in (I), O3···C10 ($1-x, y-1/2, 3/2-z$) resembles their perpendicular interaction, and its O···C distance 3.387 (2)Å is near the mean distance they report. However, the O atom in this interaction is actually nearer the methyl C [O3···C11 = 3.267 (2) Å].

Experimental

In accordance with previously described preparative methods (Knoevenagel *et al.*, 1903; Wilson, 1963), a mixture of 40 ml acetylacetone (0.39 mol) and 13.5 ml of formaldehyde (37% aqueous solution; 0.18 mol) was stirred for 5 days. The product separated on standing into a gold-colored organic bottom layer (40 ml) and a pale-yellow aqueous top layer (10 ml). The organic layer was dried over $MgSO_4$ and an equal volume of diethyl ether was added. The resulting solution was cooled in a dry ice-acetone bath to produce a white solid. After repeatedly taking up the viscous portions in a minimum of diethyl ether and cooling in the dry ice-acetone bath, a total of 11.0 g (0.052 mole, 26% yield) of crystalline solid, mp 39.5–41.0 °C, was isolated. X-ray quality crystals were obtained by cooling a solution in diethyl ether in a dry ice-acetone bath.

Refinement

H atoms were placed in idealized positions with C—H distances 0.98 − 1.00 Å and thereafter treated as riding. U_{iso} for H was assigned as 1.2 times U_{eq} of the attached C atoms (1.5 for methyl). A torsional parameter was refined for each methyl group. The absolute structure could not be determined, and Friedel pairs were averaged.

Figures

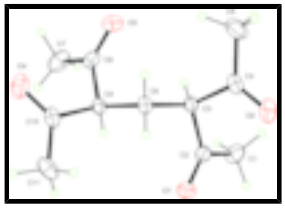

Fig. 1. Numbering scheme and ellipsoids at the 50% level. H atoms are represented with arbitrary radius.

3,5-Diacetylheptane-2,6-dione

Crystal data

$C_{11}H_{16}O_4$	$D_x = 1.203$ Mg m^{-3}
$M_r = 212.24$	Melting point: 313.5-314.0 K
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
Hall symbol: P 2ac 2ab	Cell parameters from 2556 reflections
$a = 7.810$ (2) Å	$\theta = 2.5$–33.7º
$b = 8.611$ (2) Å	$\mu = 0.09$ mm^{-1}
$c = 17.431$ (4) Å	$T = 100$ K
$V = 1172.3$ (5) Å^3	Fragment, colourless
$Z = 4$	0.47 × 0.43 × 0.40 mm
$F_{000} = 456$	

Data collection

Nonius KappaCCD (with Oxford Cryostream) diffractometer	2352 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	$R_{int} = 0.016$
Monochromator: graphite	$\theta_{max} = 33.7$º
$T = 100$ K	$\theta_{min} = 2.8$º
ω scans with κ offsets	$h = -11\rightarrow11$
Absorption correction: none	$k = -13\rightarrow13$
15692 measured reflections	$l = -27\rightarrow27$
2647 independent reflections	

Refinement

Refinement on F^2	H-atom parameters constrained
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0668P)^2 + 0.1309P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.041$	$(\Delta/\sigma)_{max} = 0.006$
$wR(F^2) = 0.113$	$\Delta\rho_{max} = 0.29$ e Å^{-3}
$S = 1.04$	$\Delta\rho_{min} = -0.18$ e Å^{-3}
2647 reflections	Extinction correction: none
140 parameters	
Primary atom site location: structure-invariant direct methods	
Secondary atom site location: difference Fourier map	
Hydrogen site location: inferred from neighbouring sites	

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 $F^2 > 2\text{sigma}(F^2)$ 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	0.05730 (14)	0.48942 (13)	0.67423 (5)	0.0284 (2)
O2	−0.06423 (14)	0.21860 (16)	0.54715 (7)	0.0388 (3)
O3	0.52584 (15)	0.07629 (14)	0.65558 (6)	0.0346 (3)
O4	0.45874 (17)	0.10347 (15)	0.84527 (6)	0.0383 (3)
C1	0.1592 (2)	0.53906 (18)	0.54771 (8)	0.0296 (3)
H1A	0.0884	0.6328	0.5508	0.044*
H1B	0.1286	0.4802	0.5016	0.044*
H1C	0.2803	0.5686	0.5452	0.044*
C2	0.12923 (16)	0.44037 (15)	0.61741 (7)	0.0212 (2)
C3	0.19679 (15)	0.27436 (14)	0.61312 (6)	0.0184 (2)
H3	0.3141	0.2768	0.5901	0.022*
C4	0.08071 (18)	0.17786 (17)	0.56105 (7)	0.0246 (2)
C5	0.1554 (2)	0.03050 (19)	0.52954 (9)	0.0366 (3)
H5A	0.0644	−0.0469	0.5234	0.055*
H5B	0.2423	−0.0092	0.5650	0.055*
H5C	0.2082	0.0514	0.4796	0.055*
C6	0.20811 (15)	0.19736 (15)	0.69250 (6)	0.0195 (2)
H6A	0.1052	0.2245	0.7228	0.023*
H6B	0.2105	0.0831	0.6863	0.023*
C7	0.69870 (18)	0.2565 (2)	0.72430 (11)	0.0348 (3)
H7A	0.7860	0.1755	0.7298	0.052*
H7B	0.6838	0.3103	0.7734	0.052*
H7C	0.7351	0.3310	0.6851	0.052*
C8	0.53220 (16)	0.18388 (16)	0.70076 (7)	0.0231 (2)
C9	0.36884 (15)	0.24996 (14)	0.73593 (6)	0.0182 (2)
H9	0.3751	0.3659	0.7337	0.022*
C10	0.36087 (17)	0.20085 (16)	0.82022 (7)	0.0236 (2)
C11	0.22526 (19)	0.27536 (18)	0.86857 (7)	0.0294 (3)
H11A	0.2417	0.2456	0.9223	0.044*
H11B	0.1122	0.2407	0.8512	0.044*
H11C	0.2332	0.3885	0.8638	0.044*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0318 (5)	0.0291 (5)	0.0243 (4)	0.0065 (4)	0.0051 (4)	−0.0015 (4)
O2	0.0300 (5)	0.0493 (7)	0.0371 (6)	0.0006 (5)	−0.0138 (5)	−0.0062 (5)
O3	0.0336 (5)	0.0348 (6)	0.0354 (5)	0.0123 (5)	−0.0005 (4)	−0.0080 (5)
O4	0.0445 (7)	0.0436 (6)	0.0269 (5)	0.0058 (6)	−0.0062 (5)	0.0120 (4)
C1	0.0315 (6)	0.0299 (6)	0.0275 (6)	0.0059 (5)	0.0050 (5)	0.0104 (5)
C2	0.0197 (5)	0.0237 (5)	0.0201 (4)	0.0015 (4)	−0.0005 (4)	0.0018 (4)
C3	0.0182 (5)	0.0219 (5)	0.0152 (4)	0.0000 (4)	−0.0008 (4)	−0.0002 (4)
C4	0.0287 (6)	0.0280 (6)	0.0169 (4)	−0.0038 (5)	−0.0027 (4)	−0.0007 (4)
C5	0.0404 (8)	0.0341 (7)	0.0353 (7)	−0.0033 (7)	−0.0031 (6)	−0.0142 (6)
C6	0.0203 (5)	0.0220 (5)	0.0163 (4)	−0.0024 (4)	−0.0024 (4)	0.0018 (4)
C7	0.0203 (6)	0.0335 (7)	0.0506 (9)	−0.0010 (6)	−0.0019 (6)	0.0075 (7)
C8	0.0211 (5)	0.0231 (5)	0.0250 (5)	0.0033 (5)	−0.0009 (4)	0.0053 (4)
C9	0.0197 (4)	0.0184 (4)	0.0165 (4)	−0.0011 (4)	−0.0014 (4)	0.0012 (4)
C10	0.0283 (6)	0.0249 (5)	0.0175 (4)	−0.0066 (5)	−0.0043 (4)	0.0018 (4)
C11	0.0338 (7)	0.0348 (7)	0.0198 (5)	−0.0117 (6)	0.0050 (5)	−0.0036 (5)

Geometric parameters (Å, °)

O1—C2	1.2145 (15)	C5—H5C	0.9800
O2—C4	1.2097 (18)	C6—C9	1.5343 (16)
O3—C8	1.2169 (18)	C6—H6A	0.9900
O4—C10	1.2158 (17)	C6—H6B	0.9900
C1—C2	1.5011 (18)	C7—C8	1.500 (2)
C1—H1A	0.9800	C7—H7A	0.9800
C1—H1B	0.9800	C7—H7B	0.9800
C1—H1C	0.9800	C7—H7C	0.9800
C2—C3	1.5256 (17)	C8—C9	1.5256 (18)
C3—C4	1.5284 (17)	C9—C10	1.5301 (17)
C3—C6	1.5370 (16)	C9—H9	1.0000
C3—H3	1.0000	C10—C11	1.498 (2)
C4—C5	1.501 (2)	C11—H11A	0.9800
C5—H5A	0.9800	C11—H11B	0.9800
C5—H5B	0.9800	C11—H11C	0.9800
C2—C1—H1A	109.5	C9—C6—H6B	109.4
C2—C1—H1B	109.5	C3—C6—H6B	109.4
H1A—C1—H1B	109.5	H6A—C6—H6B	108.0
C2—C1—H1C	109.5	C8—C7—H7A	109.5
H1A—C1—H1C	109.5	C8—C7—H7B	109.5
H1B—C1—H1C	109.5	H7A—C7—H7B	109.5
O1—C2—C1	122.37 (12)	C8—C7—H7C	109.5
O1—C2—C3	121.72 (11)	H7A—C7—H7C	109.5
C1—C2—C3	115.90 (10)	H7B—C7—H7C	109.5
C2—C3—C4	109.48 (10)	O3—C8—C7	121.98 (13)
C2—C3—C6	112.33 (10)	O3—C8—C9	120.65 (12)

C4—C3—C6	109.52 (10)	C7—C8—C9	117.37 (12)
C2—C3—H3	108.5	C8—C9—C10	108.47 (10)
C4—C3—H3	108.5	C8—C9—C6	112.08 (10)
C6—C3—H3	108.5	C10—C9—C6	111.04 (10)
O2—C4—C5	122.38 (14)	C8—C9—H9	108.4
O2—C4—C3	121.09 (13)	C10—C9—H9	108.4
C5—C4—C3	116.53 (12)	C6—C9—H9	108.4
C4—C5—H5A	109.5	O4—C10—C11	122.55 (12)
C4—C5—H5B	109.5	O4—C10—C9	120.66 (12)
H5A—C5—H5B	109.5	C11—C10—C9	116.78 (11)
C4—C5—H5C	109.5	C10—C11—H11A	109.5
H5A—C5—H5C	109.5	C10—C11—H11B	109.5
H5B—C5—H5C	109.5	H11A—C11—H11B	109.5
C9—C6—C3	111.34 (9)	C10—C11—H11C	109.5
C9—C6—H6A	109.4	H11A—C11—H11C	109.5
C3—C6—H6A	109.4	H11B—C11—H11C	109.5
O1—C2—C3—C4	106.19 (14)	O3—C8—C9—C10	107.67 (13)
C1—C2—C3—C4	−74.56 (13)	C7—C8—C9—C10	−72.17 (14)
O1—C2—C3—C6	−15.71 (16)	O3—C8—C9—C6	−15.27 (16)
C1—C2—C3—C6	163.54 (11)	C7—C8—C9—C6	164.88 (12)
C2—C3—C4—O2	−20.20 (17)	C3—C6—C9—C8	−70.39 (13)
C6—C3—C4—O2	103.37 (14)	C3—C6—C9—C10	168.12 (10)
C2—C3—C4—C5	160.62 (12)	C8—C9—C10—O4	−11.25 (17)
C6—C3—C4—C5	−75.80 (14)	C6—C9—C10—O4	112.32 (14)
C2—C3—C6—C9	−79.56 (12)	C8—C9—C10—C11	170.22 (11)
C4—C3—C6—C9	158.56 (10)	C6—C9—C10—C11	−66.21 (14)

Fig. 1