organic compounds

2,5-Dihydroxy-2,5-dimethylcyclohexane-1,4-dione

Igor V. Nikolaenko,[a]* Carla Bazzicalupi,[b] Craig Grimmer[a] and Ashen Bhagwandin[a]

[a]School of Chemistry, University of KwaZulu-Natal, Private Bag X01, Scottsville, Pietermaritzburg 3209, South Africa, and [b]Department of Chemistry, University of Florence, Via della Lastruccia 3, 50019 Sesto Fiorentino, Florence, Italy
Correspondence e-mail: nikolaenko@ukzn.ac.za

The title compound, $C_8H_{12}O_4$, was synthesized and characterized by mp, FT–IR, NMR and single-crystal X-ray diffraction at 298 K. The molecule is centrosymmetric with the cyclohexane ring in a chair conformation; neighbouring carbonyl and alcohol groups are *cis* to each other, due to intramolecular hydrogen-bonding interactions. A number of strong and weak intermolecular hydrogen-bonding interactions are responsible for the formation of molecular sheets, which are held together by weak van der Waals forces.

Related literature

For general background on the double aldol condensation of 2,3-butanedione (diacetyl) in the presence of alkali, see: von Pechmann & Wedekind (1895); Diels *et al.* (1914). For related literature, see: Schrödinger (2007).
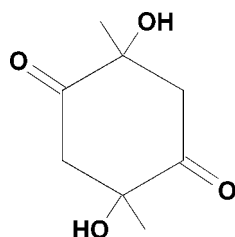
Experimental

Crystal data

$C_8H_{12}O_4$	γ = 101.82 (3)°
M_r = 172.18	V = 204.90 (15) Å^3
Triclinic, $P\bar{1}$	Z = 1
a = 5.795 (2) Å	Mo $K\alpha$ radiation
b = 6.076 (2) Å	μ = 0.11 mm^{-1}
c = 6.441 (3) Å	T = 298 K
α = 91.97 (3)°	0.25 × 0.2 × 0.05 mm
β = 111.59 (4)°	

Data collection

Oxford Diffraction PX Ultra diffractometer	1953 measured reflections
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2006)	818 independent reflections
	506 reflections with $I > 2\sigma(I)$
T_{min} = 0.967, T_{max} = 0.994	R_{int} = 0.020

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.035	57 parameters
$wR(F^2)$ = 0.083	H-atom parameters constrained
S = 0.89	$\Delta\rho_{max}$ = 0.13 e Å^{-3}
818 reflections	$\Delta\rho_{min}$ = −0.14 e Å^{-3}

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O5—H5···O6	0.82	2.24	2.669 (2)	113
O5—H5···O6^{ii}	0.82	2.25	2.999 (2)	151
C4—H4B···O5^{iii}	0.96	2.71	3.574 (3)	150

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

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2007).

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supplementary materials

2,5-Dihydroxy-2,5-dimethylcyclohexane-1,4-dione

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Comment

For the first time a possibility of double aldol condensation of 2,3-butanedione (diacetyl) in the presence of alkali into title compound (I, Fig.4), was considered by von Pechmann & Wedekind (1895). At the time the authors rejected this structure in favour of a linear "aldol" (II) on the evidence of their condensation product reacting with three equivalents of phenylhydrazine.

The matter was re-examined by Diels *et al.* (1914), who thought it unlikely for the aldol to have an asymmetric structure in view of the ease with which it can be converted into *p*-xyloquinone. Having shown that in certain conditions the condensation product reacts with two equivalents of carboxyethylisocyanate (this confirmed presence of two hydroxide groups in the molecule), they reversed original conclusion in favour of symmetric structure (I). In the 93 years of diacetyl chemistry that followed this compound has not been mentioned again.

Now we are able to confirm its existence conclusively; in this communication the molecular and crystal structure of (I), determined by a single-crystal X-ray diffraction, is presented.

Our recent work on the oligomerization of diacetyl in a variety of conditions established that the process is a rather complex one. The first stage of a base-catalysed oligomerization, if arrested eary, affords a mixture of dimers, among which are both (I) and (II), two structural isomers of 5-acetyl-2-hydroxy-2,5-dimethyldihydrofurane-3(2*H*)-one (III) and (IV), as well as 2,4,5-trimethyl-2*H*-furan-3-one (V). We have separated and characterized all of the above compounds (their structure, properties, and reactivity will be reported elsewhere) but the focus of the current paper is on the symmetrical cyclohexane-dione (I).

Molecular Structure: The molecule of (I) is centrosymmetric (Fig.1). The cyclohexane ring is in a chair conformation with neighbouring carbonyl and alcohol groups *cis* to each other, probably, due to the intramolecular hydrogen bonding interactions (O5···O6: 2.669 (2) Å, O5—H5···O6: 113 °). C_i symmetry of this molecule is retained in solution according to our one-dimensional and two-dimensional NMR studies. *Ab initio* DFT calculations in vacuum (*Jaguar* and *Maestro*; Schrödinger, 2007), confirmed that the solid state structure of (I) is indeed the lowest energy conformer for this molecule. Geometric parameters, some of which are given in Table 1, are representative of cyclic alkanes.

Crystal Structure: A packing diagram for the crystal structure of (I) is shown in Fig. 2. The spacial arrangement of molecules is shaped up by a set of eight strong and weak hydrogen bonding interactions (Table 2). Head-to-tail hydrogen bonding of the hydroxide and carbonyl groups afford parallel molecular chains (Fig. 3a). The latter are cross-linked by weak hydrogen bonding of a methyl group proton to the hydroxy group oxygen (Fig. 3 b), yielding molecular sheets (Fig. 3c). Weak van der Waals interactions hold a stack of such sheets together; the interplanar distance within the stack is 4.471 Å.

supplementary materials

Experimental

The title compound was synthesized following the procedure similar to that of von Pechmann & Wedekind (1895). The product mixture was extracted with ether for 24 h. After the removal of the solvent, the resulting amber oil was distilled at reduced pressure; the fraction with bp of 92.5 °C at 2.5 mbar was collected and eventually deposited colourless well shaped prisms of (I). The crystals were washed with hexane and characterized by melting point determination, FTIR, NMR, and X-ray diffraction.

Melting point temperature. Reichert apparatus.

176.2–176.5 °C.

FTIR. Perkin-Elmer Spectrum One.

(KBr, cm^{-1}): 1653 $v(A_u, C=O)$, 1714 $v(A_g, C=O)$, 2925, 2969, 2989 $v(C–H)$, 3420 $v(A_g, O–H)$, 3483 $v(A_u, O–H)$.

NMR. Varian Unity Inova 500, Oxford magnet 11.744 T.

^{1}H NMR (CDCl$_3$, 499.98 MHz), δ: 1.381 (s, 6H, CH$_3$, C4), 2.936 (d, 2H, ^{2}J = 14.291 Hz, CH$_2$, C2), 3.004 (d, 2H, ^{2}J = 14.291 Hz, CH$_2$, C2), 3.949 (s, 2H, OH).

^{13}C NMR (CDCl$_3$, 125.736 MHz), δ: 26.709 (CH$_3$, C4), 49.292 (CH$_2$, C2), about 77 (masked by CDCl$_3$, C1), 207.649 (C3).

Melting points were measured with the thermometer calibrated against melting points of the AR grade benzoic, salicylic, and succinic acid.

Assignment of chemical shifts in the NMR-spectra is based on the analysis of one-dimensional and correlation two-dimensional spectra (ghmqc, ghsqc, noesy).

Refinement

Hydrogen atoms were introduced in calculated positions with O—H = 0.82 Å and C—H = 0.0.96–0.97 Å, and with $U_{iso}(H)$ = 1.5 $U_{eq}(C, O)$ or 1.5 $U_{eq}(C)$ for methylene H atoms.
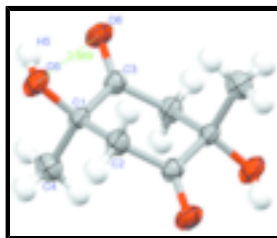
Figures

Fig. 1. A view of the molecular structure of the title compound. Unlabelled atoms are related to the labelled ones by (2 − x, 1 − y, 2 − z). Displacement ellipsoids (Mercury 1.4.2) are drawn at the 50% probability level.
Fig. 2. Packing diagram approximately viewed down b-axis.
Fig. 3 (a). Strong O—H⋯O hydrogen bonding interactions responsible for the formation of molecular chains. (b) Weak C—H⋯O hydrogen bonding interactions in the crystal structure. (c) Molecular sheets shaped up by the strong and weak hydrogen bonding interactons.
Fig. 4. Identified products of a base-catalysed dimerization of diacetyl.
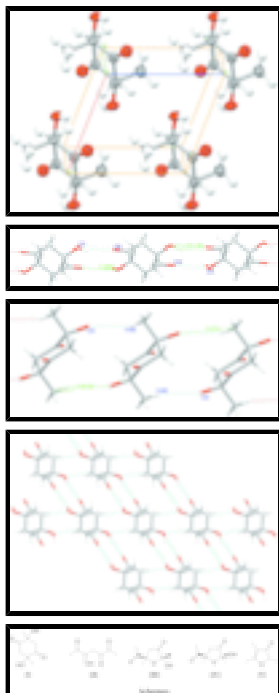
2,5-Dihydroxy-2,5-dimethylcyclohexane-1,4-dione

Crystal data

$C_8H_{12}O_4$	$Z = 1$
$M_r = 172.18$	$F_{000} = 92$
Triclinic, $P\overline{1}$	$D_x = 1.395$ Mg m^{-3}
Hall symbol: -P 1	Melting point: 176.5 K
$a = 5.795$ (2) Å	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$b = 6.076$ (2) Å	Cell parameters from 840 reflections
$c = 6.441$ (3) Å	$\theta = 3.9–28.4°$
$\alpha = 91.97$ (3)°	$\mu = 0.11$ mm^{-1}
$\beta = 111.59$ (4)°	$T = 298$ K
$\gamma = 101.82$ (3)°	Prismatic, colourless
$V = 204.90$ (15) Å^3	$0.25 \times 0.2 \times 0.05$ mm

Data collection

Oxford Diffraction PX Ultra diffractometer	818 independent reflections
Radiation source: fine-focus sealed tube	506 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.020$
$T = 298$ K	$\theta_{max} = 26.4°$
ω scans	$\theta_{min} = 3.9°$
Absorption correction: multi-scan (CrysAlis RED; Oxford Diffraction, 2006)	$h = -7 \rightarrow 7$

supplementary materials

$T_{min} = 0.967$, $T_{max} = 0.994$

1953 measured reflections

$k = -7 \rightarrow 7$

$l = -7 \rightarrow 8$

Refinement

Refinement on F^2	H-atom parameters constrained
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0508P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.035$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.083$	$\Delta\rho_{max} = 0.13$ e Å^{-3}
$S = 0.89$	$\Delta\rho_{min} = -0.14$ e Å^{-3}
818 reflections	Extinction correction: none
57 parameters	

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 is 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	$U_{iso}*/U_{eq}$
O5	0.49211 (17)	0.27663 (17)	0.75565 (18)	0.0446 (3)
H5	0.4642	0.1583	0.8092	0.067*
O6	0.8000 (2)	0.11944 (17)	1.10837 (18)	0.0466 (4)
C1	0.7591 (2)	0.3570 (2)	0.8178 (2)	0.0311 (4)
C2	0.8150 (3)	0.6174 (2)	0.8484 (3)	0.0362 (4)
H2A	0.7500	0.6699	0.7021	0.043*
H2B	0.7248	0.6647	0.9360	0.043*
C3	0.9054 (3)	0.2729 (2)	1.0362 (2)	0.0318 (4)
C4	0.8370 (3)	0.2715 (3)	0.6325 (3)	0.0453 (4)
H4A	0.8053	0.1093	0.6197	0.068*
H4B	1.0154	0.3346	0.6697	0.068*
H4C	0.7391	0.3172	0.4920	0.068*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O5	0.0261 (6)	0.0444 (7)	0.0532 (7)	−0.0011 (5)	0.0082 (5)	0.0111 (6)
O6	0.0446 (7)	0.0378 (6)	0.0509 (7)	−0.0036 (5)	0.0171 (6)	0.0143 (5)

C1	0.0217 (8)	0.0307 (8)	0.0363 (9)	−0.0001 (6)	0.0091 (7)	0.0039 (7)
C2	0.0324 (9)	0.0330 (8)	0.0387 (9)	0.0071 (6)	0.0086 (7)	0.0077 (7)
C3	0.0340 (8)	0.0255 (8)	0.0352 (9)	0.0045 (7)	0.0142 (7)	0.0013 (7)
C4	0.0477 (10)	0.0469 (9)	0.0398 (9)	0.0083 (8)	0.0168 (8)	0.0011 (8)

Geometric parameters (Å, °)

O5—C1	1.419 (2)	C2—C3^{i}	1.503 (2)
O5—H5	0.8200	C2—H2A	0.9700
O6—C3	1.210 (1)	C2—H2B	0.9700
C1—C3	1.519 (2)	C4—H4A	0.9600
C1—C4	1.532 (2)	C4—H4B	0.9600
C1—C2	1.539 (2)	C4—H4C	0.9600
C1—O5—H5	109.5	C1—C2—H2B	109.0
O5—C1—C3	110.6 (1)	H2A—C2—H2B	107.8
O5—C1—C4	109.5 (1)	O6—C3—C2^{i}	122.2 (1)
C3—C1—C4	108.8 (1)	O6—C3—C1	120.6 (1)
O5—C1—C2	106.9 (1)	C2^{i}—C3—C1	117.2 (1)
C3—C1—C2	110.0 (1)	C1—C4—H4A	109.5
C4—C1—C2	111.0 (1)	C1—C4—H4B	109.5
C3^{i}—C2—C1	113.0 (1)	H4A—C4—H4B	109.5
C3^{i}—C2—H2A	109.0	C1—C4—H4C	109.5
C1—C2—H2A	109.0	H4A—C4—H4C	109.5
C3^{i}—C2—H2B	109.0	H4B—C4—H4C	109.5
O5—C1—C2—C3^{i}	167.1 (1)	C2—C1—C3—O6	133.0 (1)
C3—C1—C2—C3^{i}	47.0 (2)	O5—C1—C3—C2^{i}	−167.0 (1)
C4—C1—C2—C3^{i}	−73.5 (2)	C4—C1—C3—C2^{i}	72.7 (2)
O5—C1—C3—O6	15.2 (2)	C2—C1—C3—C2^{i}	−49.1 (2)
C4—C1—C3—O6	−105.2 (2)		

Symmetry codes: (i) −*x*+2, −*y*+1, −*z*+2.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O5—H5···O6	0.82	2.24	2.669 (2)	113
O5—H5···O6^{ii}	0.82	2.25	2.999 (2)	151
C4—H4B···O5^{iii}	0.96	2.71	3.574 (3)	150

Symmetry codes: (ii) −*x*+1, −*y*, −*z*+2; (iii) *x*+1, *y*, *z*.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

(I)   (II)   (III)   (IV)   (V)

Schemes