

3,3'-[(1*E*,1'*E*)-Hydrazine-1,2-diylidenebis(ethan-1-yl-1-ylidene)]bis(4-hydroxy-6-methyl-2*H*-pyran-2-one)

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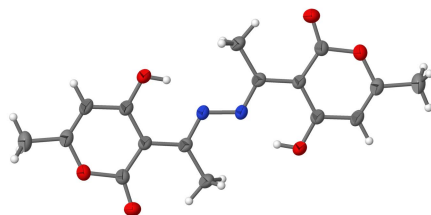
CCDC reference: 1956978

Structural data: full structural data are available from iucrdata.iucr.org

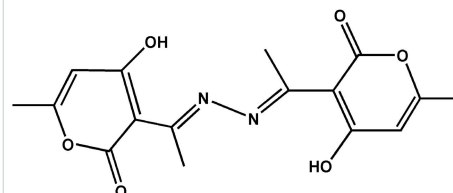
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The title compound, C₁₆H₁₆N₂O₆, lies about an inversion centre at the mid-point of the N–N bond. The molecule features two intramolecular O–H···N and two C–H···O hydrogen bonds, each of which forms an *S*(6) ring motif. In the crystal, molecules are linked by C–H···O hydrogen bonds into infinite zigzag chains propagating along the *c*-axis direction. π – π stacking interactions between the pyrone rings [centroid–centroid distances = 3.975 (2) Å] stack the molecules along *b*.

3D view



Chemical scheme



Structure description

The condensation of primary amine with several lactones has been reported. Ammonia and primary amines react with 2-pyrones to afford the corresponding 2-pyridones (Castillo *et al.*, 1982; Wang *et al.*, 1971; Djerrari *et al.*, 1993; El Kihel *et al.*, 1999; Djerrari *et al.*, 2002). Other authors have investigated the condensation of bis-nucleophiles with 4-hydroxy-6-methyl-2-pyrone and dehydroacetic acid (3-acetyl-4-hydroxy-6-methyl-2-pyrone) and had to postulate a ring opening of these pyrones to account for the experimental results (El Abbassi *et al.*, 1997; Fettouhi *et al.*, 1996; El Abbassi *et al.*, 1989). Some bis-pyrone derivatives have been reported to be excellent ligands for complexation with ruthenium metal (Venkatachalam *et al.*, 2005). The present work reports the synthesis of a bis-pyrone derivative from the condensation of hydrated hydrazine with dehydroacetic acid. The NMR and mass spectra cannot confirm the structure of the

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

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O2—H2···N1	0.82	1.73	2.4659 (18)	148
C3—H3···O3 ⁱ	0.93	2.57	3.420 (2)	152
C8—H8A···O2 ⁱⁱ	0.96	2.55	3.278 (2)	133
C8—H8B···O3	0.96	2.05	2.821 (3)	136

Symmetry codes: (i) *x*, $-y + 1$, $z - \frac{1}{2}$; (ii) *x*, $-y$, $z + \frac{1}{2}$.

product (either a bis-pyrone or a bis-pyridone). In order to establish the structure of this product, single crystals were prepared for X-ray analysis.

The asymmetric unit of the title compound contains half of the molecule with the other half generated by inversion symmetry. Two strong intramolecular hydrogen bonds complete the *S*(6) ring motifs as shown in Fig. 1. All non-hydrogen atoms of the molecule are almost coplanar, the maximum deviation from the mean plane through all of the non hydrogen atoms being 0.082 (2) Å for atom C1.

In the crystal, the molecules are linked by C3—H3···O3 and C8—H8A···O2 hydrogen bonds (Table 1), forming zigzag chains running along the *c*-axis direction as shown in Fig. 2. In addition, molecules are stacked along *b* by π – π interactions between the pyridone rings with a centroid–centroid distance of 3.975 (2) Å, Fig. 3.

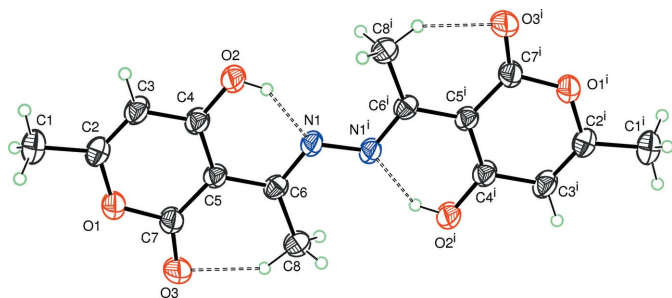


Figure 1
The title molecule with the atom-labelling scheme. The intramolecular hydrogen bonds are represented by dashed lines. Displacement ellipsoids are drawn at the 50% probability level.

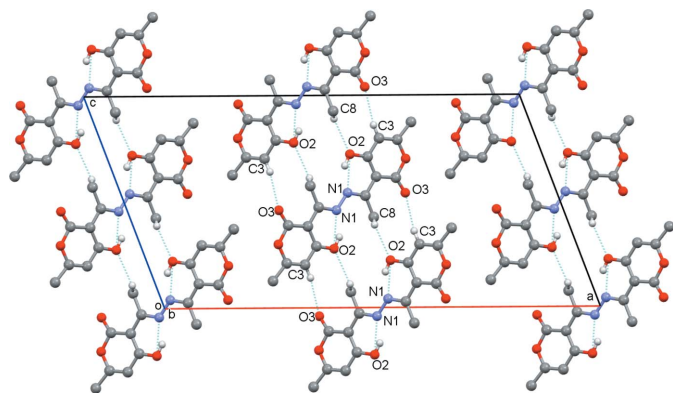


Figure 2
Projection of the title structure along (010), showing molecules connected by hydrogen bonds (dashed cyan lines). For clarity, only H atoms involved in these interactions have been included.

Table 2
Experimental details.

Crystal data	
Chemical formula	C ₁₆ H ₁₆ N ₂ O ₆
<i>M_r</i>	332.31
Crystal system, space group	Monoclinic, <i>C2/c</i>
Temperature (K)	296
<i>a</i> , <i>b</i> , <i>c</i> (Å)	27.797 (3), 3.9750 (4), 14.4569 (15)
β (°)	110.642 (4)
<i>V</i> (Å ³)	1494.8 (3)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	0.12
Crystal size (mm)	0.32 × 0.25 × 0.19
Data collection	
Diffractometer	Bruker D8 VENTURE Super DUO
Absorption correction	Multi-scan (<i>SADABS</i> ; Krause <i>et al.</i> , 2015)
<i>T_{min}</i> , <i>T_{max}</i>	0.678, 0.746
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	15395, 1627, 1221
<i>R_{int}</i>	0.043
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.641
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.050, 0.148, 1.03
No. of reflections	1627
No. of parameters	112
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å ⁻³)	0.33, -0.23

Computer programs: *APEX3* and *SAINT* (Bruker, 2016), *SHELXTL2014* (Sheldrick, 2015a), *SHELXL2018* (Sheldrick, 2015b), *WinGX* and *ORTEP-3 for Windows* (Farrugia, 2012), *Mercury* (Macrae *et al.*, 2008) and *publCIF* (Westrip, 2010).

Synthesis and crystallization

A mixture of dehydroacetic acid (20 mmol) and hydrazine monohydrate (10 mmol) was heated under reflux in *n*-butanol (30 ml) for 24 h. The solid was separated by filtration and recrystallized several times from CHCl₃ to give crystals, yield (52.1%).

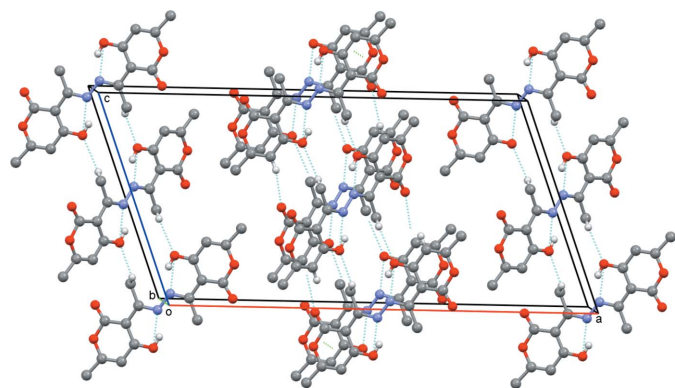


Figure 3
Crystal packing of the title compound showing molecules linked by hydrogen bonds (dashed cyan lines) and π – π interaction (green lines). For clarity, only H atoms involved in these interactions have been included.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

The authors thank the Faculty of Science, Mohammed V University in Rabat, Morocco for the X-ray measurements and Chouaib Doukkali University (El Jadida Morocco) for support.

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full crystallographic data

IUCrData (2019). 4, x191348 [https://doi.org/10.1107/S2414314619013488]

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Crystal data

C₁₆H₁₆N₂O₆

M_r = 332.31

Monoclinic, *C2/c*

a = 27.797 (3) Å

b = 3.9750 (4) Å

c = 14.4569 (15) Å

β = 110.642 (4)°

V = 1494.8 (3) Å³

Z = 4

F(000) = 696

D_x = 1.477 Mg m⁻³

Mo *Kα* radiation, λ = 0.71073 Å

Cell parameters from 1626 reflections

θ = 3.0–27.1°

μ = 0.12 mm⁻¹

T = 296 K

Block, colourless

0.32 × 0.25 × 0.19 mm

Data collection

Bruker D8 VENTURE Super DUO
diffractometer

Radiation source: INCOATEC IμS micro-focus
source

HELIOS mirror optics monochromator

Detector resolution: 10.4167 pixels mm⁻¹

φ and ω scans

Absorption correction: multi-scan
(SADABS; Krause *et al.*, 2015)

T_{min} = 0.678, *T_{max}* = 0.746

15395 measured reflections

1627 independent reflections

1221 reflections with *I* > 2σ(*I*)

R_{int} = 0.043

θ_{max} = 27.1°, θ_{min} = 3.0°

h = -34→34

k = -5→5

l = -18→18

Refinement

Refinement on *F*²

Least-squares matrix: full

R[*F*² > 2σ(*F*²)] = 0.050

wR(*F*²) = 0.148

S = 1.03

1627 reflections

112 parameters

0 restraints

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

w = 1/[σ²(*F_o*²) + (0.0725*P*)² + 1.6983*P*]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} = 0.003

Δρ_{max} = 0.33 e Å⁻³

Δρ_{min} = -0.23 e Å⁻³

Extinction correction: SHELXL-2018/3

(Sheldrick, 2015b),

*F_c** = *kF_c*[1 + 0.001 × *F_c*²λ³/sin(2θ)]^{-1/4}

Extinction coefficient: 0.009 (3)

Special details

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

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.31666 (5)	0.5614 (4)	0.29992 (10)	0.0404 (4)
O2	0.44045 (5)	0.0821 (4)	0.27764 (9)	0.0486 (5)
H2	0.462232	0.040600	0.331799	0.073*
O3	0.34743 (6)	0.5875 (5)	0.46061 (11)	0.0582 (5)
N1	0.47971 (5)	0.0522 (4)	0.45929 (10)	0.0318 (4)
C1	0.27228 (8)	0.5809 (6)	0.12749 (15)	0.0467 (6)
H1A	0.277478	0.547070	0.065932	0.070*
H1C	0.265360	0.814272	0.134436	0.070*
H1B	0.243653	0.447745	0.128495	0.070*
C2	0.31917 (7)	0.4781 (5)	0.21031 (13)	0.0340 (5)
C3	0.35979 (7)	0.3216 (5)	0.20315 (13)	0.0365 (5)
H3	0.360757	0.268689	0.141167	0.044*
C4	0.40194 (7)	0.2338 (5)	0.28963 (13)	0.0331 (5)
C5	0.40009 (6)	0.3095 (5)	0.38391 (12)	0.0289 (4)
C6	0.44140 (7)	0.2111 (5)	0.47291 (12)	0.0286 (4)
C7	0.35581 (7)	0.4878 (5)	0.38895 (13)	0.0350 (5)
C8	0.44100 (8)	0.2785 (6)	0.57414 (14)	0.0462 (6)
H8A	0.445878	0.071299	0.610416	0.069*
H8B	0.408612	0.375886	0.569385	0.069*
H8C	0.468260	0.431695	0.607768	0.069*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0338 (7)	0.0534 (9)	0.0312 (7)	0.0104 (6)	0.0080 (6)	0.0023 (6)
O2	0.0377 (8)	0.0835 (12)	0.0236 (6)	0.0184 (8)	0.0095 (6)	−0.0017 (7)
O3	0.0504 (9)	0.0911 (13)	0.0341 (8)	0.0279 (9)	0.0161 (7)	−0.0045 (8)
N1	0.0281 (8)	0.0433 (10)	0.0218 (7)	0.0037 (6)	0.0061 (6)	0.0014 (6)
C1	0.0391 (11)	0.0533 (14)	0.0381 (11)	0.0050 (10)	0.0015 (9)	0.0075 (10)
C2	0.0328 (10)	0.0379 (11)	0.0279 (9)	−0.0028 (8)	0.0063 (7)	0.0045 (8)
C3	0.0352 (10)	0.0510 (13)	0.0216 (8)	−0.0004 (9)	0.0078 (7)	0.0028 (8)
C4	0.0299 (9)	0.0440 (11)	0.0253 (9)	0.0002 (8)	0.0096 (7)	0.0012 (8)
C5	0.0289 (9)	0.0348 (10)	0.0231 (8)	0.0006 (7)	0.0092 (7)	0.0008 (7)
C6	0.0307 (9)	0.0319 (10)	0.0239 (8)	−0.0024 (7)	0.0105 (7)	0.0006 (7)
C7	0.0314 (9)	0.0432 (11)	0.0294 (9)	0.0046 (8)	0.0095 (7)	0.0027 (8)
C8	0.0489 (12)	0.0662 (15)	0.0236 (9)	0.0188 (11)	0.0130 (8)	0.0027 (9)

Geometric parameters (Å, °)

O1—C2	1.363 (2)	C2—C3	1.325 (3)
O1—C7	1.392 (2)	C3—C4	1.423 (2)
O2—C4	1.293 (2)	C3—H3	0.9300
O2—H2	0.8200	C4—C5	1.414 (2)
O3—C7	1.206 (2)	C5—C6	1.444 (2)
N1—C6	1.311 (2)	C5—C7	1.444 (3)
N1—N1 ⁱ	1.376 (3)	C6—C8	1.492 (2)
C1—C2	1.483 (3)	C8—H8A	0.9600
C1—H1A	0.9600	C8—H8B	0.9600
C1—H1C	0.9600	C8—H8C	0.9600
C1—H1B	0.9600		
C2—O1—C7	122.85 (15)	C5—C4—C3	119.73 (17)
C4—O2—H2	109.5	C4—C5—C6	120.89 (16)
C6—N1—N1 ⁱ	118.75 (18)	C4—C5—C7	118.31 (16)
C2—C1—H1A	109.5	C6—C5—C7	120.80 (15)
C2—C1—H1C	109.5	N1—C6—C5	115.43 (15)
H1A—C1—H1C	109.5	N1—C6—C8	121.41 (16)
C2—C1—H1B	109.5	C5—C6—C8	123.15 (16)
H1A—C1—H1B	109.5	O3—C7—O1	113.60 (16)
H1C—C1—H1B	109.5	O3—C7—C5	129.10 (17)
C3—C2—O1	121.28 (16)	O1—C7—C5	117.30 (15)
C3—C2—C1	126.66 (18)	C6—C8—H8A	109.5
O1—C2—C1	112.07 (17)	C6—C8—H8B	109.5
C2—C3—C4	120.47 (17)	H8A—C8—H8B	109.5
C2—C3—H3	119.8	C6—C8—H8C	109.5
C4—C3—H3	119.8	H8A—C8—H8C	109.5
O2—C4—C5	122.80 (16)	H8B—C8—H8C	109.5
O2—C4—C3	117.46 (16)		
C7—O1—C2—C3	-0.3 (3)	N1 ⁱ —N1—C6—C8	-0.2 (3)
C7—O1—C2—C1	179.27 (17)	C4—C5—C6—N1	0.4 (3)
O1—C2—C3—C4	0.5 (3)	C7—C5—C6—N1	-179.64 (17)
C1—C2—C3—C4	-179.1 (2)	C4—C5—C6—C8	-178.80 (18)
C2—C3—C4—O2	-179.86 (19)	C7—C5—C6—C8	1.2 (3)
C2—C3—C4—C5	1.0 (3)	C2—O1—C7—O3	178.35 (18)
O2—C4—C5—C6	-1.6 (3)	C2—O1—C7—C5	-1.2 (3)
C3—C4—C5—C6	177.46 (17)	C4—C5—C7—O3	-176.9 (2)
O2—C4—C5—C7	178.38 (19)	C6—C5—C7—O3	3.1 (3)
C3—C4—C5—C7	-2.5 (3)	C4—C5—C7—O1	2.6 (3)
N1 ⁱ —N1—C6—C5	-179.43 (19)	C6—C5—C7—O1	-177.38 (16)

Symmetry code: (i) $-x+1, -y, -z+1$.

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
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