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5,5-Diphenyl-*cis*-penta-2,4-dienoic acid

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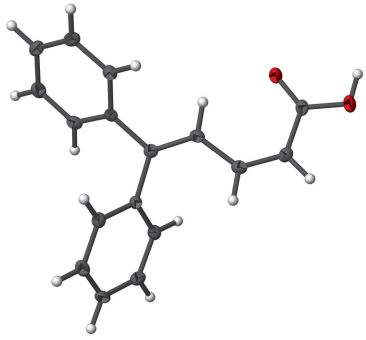
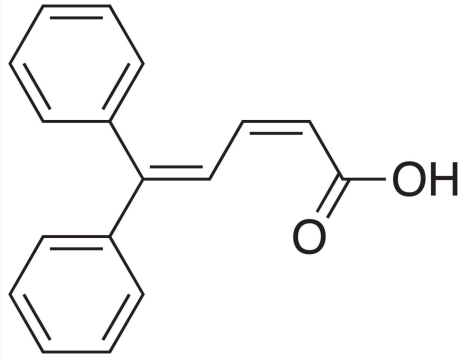
Structural data: full structural data are available from iucrdata.iucr.org

In the title compound, $C_{17}H_{14}O_2$, the dihedral angle between the phenyl rings is 76.52 (7)°. In the crystal, pairwise O—H···O hydrogen bonds link the molecules into carboxylic acid inversion dimers.

3D view



Chemical scheme



Structure description

Many 2,4-dienoic acids are widely found in nature and have shown important biological activity (Masi *et al.*, 2014). For example, abscisic acid {systematic name: (2*Z*,4*E*)-5-[(1*S*)-1-hydroxy-2,6,6-trimethyl-4-oxocyclohex-2-en-1-yl]-3-methylpenta-2,4-dienoic acid}, the most common 2,4-pentadienoic acid, isolated from cotton fruit (Ohkuma *et al.*, 1963), is a plant hormone that plays important developmental processes (Finkelstein 2013). It also plays an important role in plant responses to environmental stress and plant pathogens (Zhu, 2002; Seo & Koshiba 2002). Many methods for the synthesis of this diene system in pent-2,4-dienoic acids have been developed (Huh *et al.*, 1993; Bellassoued & Ennigrou 1991). In this paper we report a new methodology for the synthesis of the title compound, **1**, and its crystal structure.

The crystal structure of **1** has monoclinic symmetry with one molecule in the asymmetric unit: the molecular structure contains two conjugated carbon double bonds (C1═C14) and (C15═C16) in which the former diene fragment at C1 bound to two phenyl-ring substituents and the latter diene moiety further binds at C16 to a carboxylic acid functional group leading to a *cis* configuration (Fig. 1). The bond lengths of the diene arrangements C1═C14 and C15═C16 are 1.349 (2) Å and 1.346 (2) Å, respectively. The carboxyl group has the following bond lengths: C17—O1 [1.228 (2) Å] and C17—O2 [1.324 (2) Å]. In the crystal, pairwise O2—H2···O1 hydrogen-bonding interactions form dimeric arrangements between molecules, forming a loop with an $R_2^2(8)$ graph-set motif (Fig. 2 and Table 1).

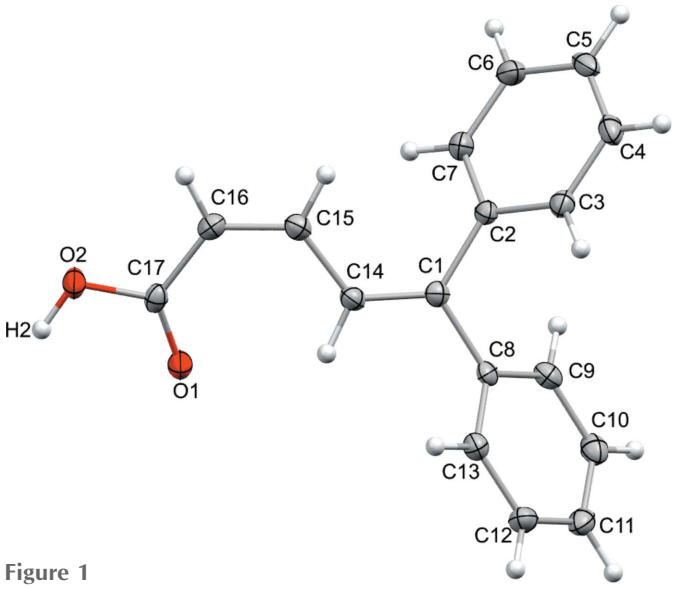


Figure 1
The title molecule with 50% probability ellipsoids.

Synthesis and crystallization

The reaction of propargyl bromide, **2**, with *n*-BuLi in the presence of tetramethylethylenediamine (TMEDA), at −78°C, generated the synthetic equivalent of the dianion 1,3-dilithiopropyne, **3**, Fig. 3 (Cabezas *et al.*, 2001). Sequential treatment of this dianion, **3**, with benzophenone followed by addition of ethyl chloroformate, and warming to room temperature overnight, produced carbonate, **4**, in 70% yield. Alkaline hydrolysis of **4**, using KOH in methanol, at room temperature for 3 h yielded 5,5-diphenylpent-4-ene-2-ynoic acid, **5**, in 87% yield. Hydrogenation of **5**, using Lindlar's catalyst yielded 5,5-diphenyl-*cis*-penta-2,4-dienoic acid, **1**, in 97% isolated yield. The overall yield for this synthesis was 59%. Light-yellow blocks were recrystallized from ethyl acetate solution at ambient temperature.

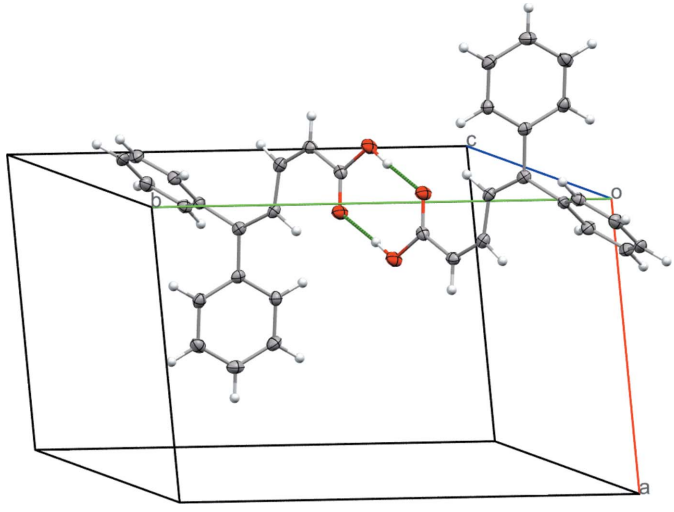


Figure 2
Packing of the molecules with O—H···O hydrogen bonds shown as green dashed lines.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2···O1^{i}	0.93	1.74	2.6628 (14)	177

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{17}H_{14}O_2$
M_r	250.29
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	100
a, b, c (Å)	9.0801 (4), 15.4598 (7), 10.0920 (4)
β (°)	109.453 (1)
V (Å^3)	1335.81 (10)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.08
Crystal size (mm)	0.25 × 0.15 × 0.10
Data collection	
Diffractometer	Bruker D8 Venture
Absorption correction	Multi-scan (*SADABS*; Bruker, 2015)
T_{min}, T_{max}	0.713, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	19268, 3081, 2479
R_{int}	0.037
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.651
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.045, 0.101, 1.05
No. of reflections	3081
No. of parameters	174
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.25, −0.33

Computer programs: *APEX3* and *SAINT* (Bruker, 2015), *SHELXT* (Sheldrick 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*) and *Mercury* (Macrae *et al.*, 2006).

Refinement

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

Acknowledgements

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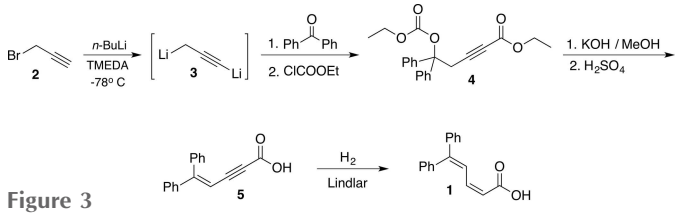

Figure 3
A synthetic scheme for the preparation of the title compound.

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full crystallographic data

IUCrData (2019). **4**, x181799 [https://doi.org/10.1107/S2414314618017996]

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Crystal data

$C_{17}H_{14}O_2$
M_r = 250.29
Monoclinic, $P2_1/n$
a = 9.0801 (4) Å
b = 15.4598 (7) Å
c = 10.0920 (4) Å
β = 109.453 (1)°
V = 1335.81 (10) Å^3
Z = 4
$F(000)$ = 528
D_x = 1.244 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 7723 reflections
θ = 2.5–27.5°
μ = 0.08 mm^{-1}
T = 100 K
Block, light yellow
0.25 × 0.15 × 0.10 mm

Data collection

Bruker D8 Venture diffractometer
Radiation source: Incoatec Microsource
Mirrors monochromator
Detector resolution: 10.4167 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2015)
T_{min} = 0.713, T_{max} = 0.746
19268 measured reflections
3081 independent reflections
2479 reflections with $I > 2\sigma(I)$
R_{int} = 0.037
θ_{max} = 27.6°, θ_{min} = 2.5°
h = −11→11
k = −20→20
l = −13→13

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.101
S = 1.05
3081 reflections
174 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 atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0392P)^2 + 0.6455P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.25 e Å^{-3}
$\Delta\rho_{min}$ = −0.33 e Å^{-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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.05901 (11)	0.54513 (7)	0.15632 (10)	0.0237 (2)
O2	−0.18489 (12)	0.50474 (7)	0.03482 (10)	0.0228 (2)
H2	−0.1377 (11)	0.4886 (11)	−0.0300 (16)	0.034*
C1	0.18364 (15)	0.64377 (9)	0.56368 (13)	0.0154 (3)
C2	0.10925 (15)	0.70128 (9)	0.64163 (14)	0.0158 (3)
C3	0.14619 (16)	0.68961 (9)	0.78666 (14)	0.0187 (3)
H3	0.2151	0.6444	0.8327	0.022*
C4	0.08313 (17)	0.74347 (10)	0.86354 (15)	0.0230 (3)
H4	0.1068	0.7341	0.9615	0.028*
C5	−0.01446 (17)	0.81101 (10)	0.79803 (16)	0.0241 (3)
H5	−0.0564	0.8484	0.8512	0.029*
C6	−0.05063 (17)	0.82382 (10)	0.65483 (16)	0.0241 (3)
H6	−0.1172	0.8702	0.6099	0.029*
C7	0.01017 (16)	0.76900 (10)	0.57661 (15)	0.0207 (3)
H7	−0.016	0.7778	0.4783	0.025*
C8	0.35685 (16)	0.63744 (9)	0.62313 (13)	0.0156 (3)
C9	0.44543 (16)	0.71162 (9)	0.67401 (14)	0.0191 (3)
H9	0.3941	0.7653	0.6724	0.023*
C10	0.60701 (17)	0.70804 (10)	0.72673 (15)	0.0224 (3)
H10	0.6658	0.7592	0.7594	0.027*
C11	0.68287 (17)	0.62948 (10)	0.73173 (15)	0.0227 (3)
H11	0.7937	0.6267	0.7676	0.027*
C12	0.59618 (17)	0.55526 (10)	0.68411 (15)	0.0219 (3)
H12	0.6479	0.5013	0.6891	0.026*
C13	0.43436 (16)	0.55893 (9)	0.62916 (14)	0.0184 (3)
H13	0.3761	0.5077	0.5955	0.022*
C14	0.10456 (16)	0.60064 (9)	0.44511 (14)	0.0168 (3)
H14	0.1645	0.5701	0.3991	0.02*
C15	−0.06333 (16)	0.59693 (9)	0.38208 (14)	0.0180 (3)
H15	−0.1222	0.6177	0.4376	0.022*
C16	−0.14545 (16)	0.56720 (9)	0.25332 (14)	0.0180 (3)
H16	−0.2558	0.5646	0.2294	0.022*
C17	−0.07883 (16)	0.53848 (9)	0.14689 (14)	0.0170 (3)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0181 (5)	0.0348 (6)	0.0173 (5)	−0.0027 (4)	0.0048 (4)	−0.0075 (4)
O2	0.0200 (5)	0.0319 (6)	0.0148 (5)	−0.0042 (4)	0.0035 (4)	−0.0056 (4)
C1	0.0170 (7)	0.0164 (7)	0.0133 (6)	0.0015 (5)	0.0058 (5)	0.0031 (5)
C2	0.0138 (7)	0.0185 (7)	0.0151 (6)	−0.0015 (5)	0.0046 (5)	−0.0031 (5)
C3	0.0170 (7)	0.0218 (7)	0.0162 (7)	−0.0013 (6)	0.0042 (5)	−0.0002 (5)
C4	0.0223 (8)	0.0321 (8)	0.0163 (7)	−0.0047 (6)	0.0086 (6)	−0.0062 (6)
C5	0.0181 (7)	0.0290 (8)	0.0283 (8)	−0.0036 (6)	0.0121 (6)	−0.0139 (6)
C6	0.0172 (7)	0.0251 (8)	0.0277 (8)	0.0047 (6)	0.0045 (6)	−0.0047 (6)

C7	0.0189 (7)	0.0254 (8)	0.0158 (7)	0.0019 (6)	0.0030 (6)	−0.0024 (6)
C8	0.0167 (7)	0.0211 (7)	0.0102 (6)	0.0010 (5)	0.0061 (5)	−0.0001 (5)
C9	0.0221 (7)	0.0190 (7)	0.0188 (7)	0.0009 (6)	0.0103 (6)	−0.0015 (5)
C10	0.0226 (8)	0.0264 (8)	0.0206 (7)	−0.0063 (6)	0.0102 (6)	−0.0046 (6)
C11	0.0156 (7)	0.0342 (9)	0.0181 (7)	0.0003 (6)	0.0053 (6)	−0.0005 (6)
C12	0.0198 (7)	0.0243 (8)	0.0210 (7)	0.0060 (6)	0.0061 (6)	0.0003 (6)
C13	0.0197 (7)	0.0191 (7)	0.0165 (7)	−0.0003 (6)	0.0061 (5)	−0.0024 (5)
C14	0.0188 (7)	0.0174 (7)	0.0151 (6)	0.0032 (5)	0.0070 (5)	0.0002 (5)
C15	0.0203 (7)	0.0171 (7)	0.0178 (7)	0.0023 (5)	0.0081 (6)	0.0009 (5)
C16	0.0147 (7)	0.0188 (7)	0.0192 (7)	0.0006 (5)	0.0041 (5)	0.0013 (5)
C17	0.0182 (7)	0.0147 (6)	0.0150 (7)	0.0001 (5)	0.0015 (5)	0.0011 (5)

Geometric parameters (Å, º)

O1—C17	1.2275 (17)	C8—C13	1.3943 (19)
O2—C17	1.3241 (16)	C8—C9	1.397 (2)
O2—H2	0.928 (19)	C9—C10	1.385 (2)
C1—C14	1.3489 (19)	C9—H9	0.95
C1—C8	1.4882 (19)	C10—C11	1.389 (2)
C1—C2	1.4898 (18)	C10—H10	0.95
C2—C7	1.394 (2)	C11—C12	1.384 (2)
C2—C3	1.4000 (19)	C11—H11	0.95
C3—C4	1.385 (2)	C12—C13	1.388 (2)
C3—H3	0.95	C12—H12	0.95
C4—C5	1.386 (2)	C13—H13	0.95
C4—H4	0.95	C14—C15	1.444 (2)
C5—C6	1.385 (2)	C14—H14	0.95
C5—H5	0.95	C15—C16	1.3455 (19)
C6—C7	1.392 (2)	C15—H15	0.95
C6—H6	0.95	C16—C17	1.466 (2)
C7—H7	0.95	C16—H16	0.95
C17—O2—H2	109.5	C10—C9—H9	119.5
C14—C1—C8	120.27 (12)	C8—C9—H9	119.5
C14—C1—C2	124.22 (12)	C9—C10—C11	119.86 (14)
C8—C1—C2	115.50 (11)	C9—C10—H10	120.1
C7—C2—C3	118.77 (13)	C11—C10—H10	120.1
C7—C2—C1	122.32 (12)	C12—C11—C10	119.64 (13)
C3—C2—C1	118.83 (12)	C12—C11—H11	120.2
C4—C3—C2	120.55 (13)	C10—C11—H11	120.2
C4—C3—H3	119.7	C11—C12—C13	120.59 (14)
C2—C3—H3	119.7	C11—C12—H12	119.7
C3—C4—C5	120.22 (13)	C13—C12—H12	119.7
C3—C4—H4	119.9	C12—C13—C8	120.31 (13)
C5—C4—H4	119.9	C12—C13—H13	119.8
C6—C5—C4	119.80 (13)	C8—C13—H13	119.8
C6—C5—H5	120.1	C1—C14—C15	125.61 (13)
C4—C5—H5	120.1	C1—C14—H14	117.2

C5—C6—C7	120.24 (14)	C15—C14—H14	117.2
C5—C6—H6	119.9	C16—C15—C14	127.09 (13)
C7—C6—H6	119.9	C16—C15—H15	116.5
C6—C7—C2	120.41 (13)	C14—C15—H15	116.5
C6—C7—H7	119.8	C15—C16—C17	125.44 (13)
C2—C7—H7	119.8	C15—C16—H16	117.3
C13—C8—C9	118.58 (12)	C17—C16—H16	117.3
C13—C8—C1	121.67 (12)	O1—C17—O2	122.14 (13)
C9—C8—C1	119.75 (12)	O1—C17—C16	125.22 (12)
C10—C9—C8	121.01 (13)	O2—C17—C16	112.64 (12)
C14—C1—C2—C7	−53.4 (2)	C2—C1—C8—C9	−41.06 (17)
C8—C1—C2—C7	125.11 (14)	C13—C8—C9—C10	1.3 (2)
C14—C1—C2—C3	129.82 (15)	C1—C8—C9—C10	−178.39 (12)
C8—C1—C2—C3	−51.65 (17)	C8—C9—C10—C11	−1.2 (2)
C7—C2—C3—C4	1.1 (2)	C9—C10—C11—C12	−0.1 (2)
C1—C2—C3—C4	178.03 (13)	C10—C11—C12—C13	1.1 (2)
C2—C3—C4—C5	−1.6 (2)	C11—C12—C13—C8	−0.9 (2)
C3—C4—C5—C6	0.9 (2)	C9—C8—C13—C12	−0.3 (2)
C4—C5—C6—C7	0.2 (2)	C1—C8—C13—C12	179.43 (12)
C5—C6—C7—C2	−0.7 (2)	C8—C1—C14—C15	175.75 (13)
C3—C2—C7—C6	0.0 (2)	C2—C1—C14—C15	−5.8 (2)
C1—C2—C7—C6	−176.78 (13)	C1—C14—C15—C16	168.04 (14)
C14—C1—C8—C13	−42.21 (19)	C14—C15—C16—C17	−5.0 (2)
C2—C1—C8—C13	139.20 (13)	C15—C16—C17—O1	−7.0 (2)
C14—C1—C8—C9	137.53 (14)	C15—C16—C17—O2	173.96 (13)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2···O1^{i}	0.93	1.74	2.6628 (14)	177

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