

meso-2-Methyl-5-[2-(4-methylfuran-2-yl)-1,2-bis(prop-2-ynyl)oxy]ethyl]furan

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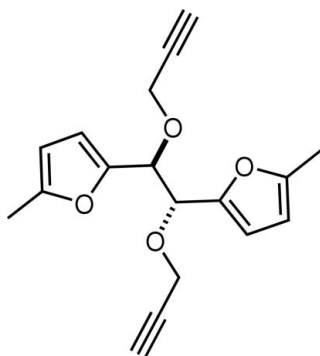
Received 5 September 2007; accepted 1 October 2007

Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.048; wR factor = 0.129; data-to-parameter ratio = 13.7.

The title compound, $\text{C}_{18}\text{H}_{18}\text{O}_4$, crystallizes with half a molecule in the asymmetric unit. The molecule is centrosymmetric and the inversion centre is located in the middle of the furfuryl C—C bond. The furan rings show an exactly parallel orientation and the alkynyl groups have a parallel orientation with respect to the furan ring systems. Intermolecular C—H \cdots O hydrogen bonds are present in the crystal structure.

Related literature

For related literature, see: Hashmi (2004, 2007); Hashmi & Hutchings (2006*a,b*); Hashmi *et al.* (2000); Hashmi, Ata *et al.* (2007); Hashmi *et al.* (2006); Hashmi, Wölfle *et al.* (2007).



Experimental

Crystal data

$\text{C}_{18}\text{H}_{18}\text{O}_4$
 $M_r = 298.32$
 Monoclinic, $P2_1/c$
 $a = 7.945$ (4) Å
 $b = 9.215$ (5) Å
 $c = 11.408$ (5) Å
 $\beta = 107.17$ (4)°

$V = 798.1$ (7) Å³
 $Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 0.09$ mm⁻¹
 $T = 293$ (2) K
 $0.9 \times 0.8 \times 0.5$ mm

Data collection

Nicolet P3 diffractometer
 Absorption correction: none
 1506 measured reflections
 1402 independent reflections
 1204 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.048$
 3 standard reflections
 every 50 reflections
 intensity decay: 3%

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.048$
 $wR(F^2) = 0.129$
 $S = 1.06$
 1402 reflections

102 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.22$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.21$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{C9}-\text{H9}\cdots\text{O2}^{\text{i}}$	0.93	2.39	3.323 (3)	179
$\text{C3}-\text{H3}\cdots\text{O1}^{\text{ii}}$	0.93	2.87	3.566 (3)	132

Symmetry codes: (i) $x, -y + \frac{3}{2}, z - \frac{1}{2}$; (ii) $x, -y + \frac{1}{2}, z - \frac{1}{2}$.

Data collection: *P3/PC Data Collection Software* (Siemens, 1991); cell refinement: *P3/PC Data Collection Software*; data reduction: *XDISK in SHELXTL-Plus* (Sheldrick, 1991); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP in SHELXTL-Plus*; software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2003).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: KP2137).

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supplementary materials

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***meso*-2-Methyl-5-[2-(4-methylfuran-2-yl)-1,2-bis(prop-2-ynyloxy)ethyl]furan**

W. Frey, M. Wölfle and A. S. K. Hashmi

Comment

In the course of the investigation of the synthetic potential of fufural derivatives as renewable feedstocks (Hashmi *et al.*, 2006; Hashmi, Ata *et al.*, 2007) we investigated their possible transformation into bis-phenols in the gold-catalyzed phenol synthesis (Hashmi *et al.*, 2000), one of the numerous gold-catalyzed cycloisomerization reactions known today (Hashmi, 2004; Hashmi & Hutchings, 2006a,b; Hashmi, 2007). This crystal structure analysis now allows an unambiguous assignment of the different diastereomers formed in previous step, the organo-catalyzed benzoin condensation of fufurals, and in the subsequent step, the gold-catalyzed synthesis of the benzoid arene ring.

The molecule crystallizes with a half of the molecule in the asymmetric unit (Fig. 1). The inversion centre located in the middle of C6—C6A ($-x + 2, -y + 1, -z + 1$) generates the molecule having the chiral centres of opposite chirality, characteristic of a *meso*-form. The perfect coplanar orientation of the two symmetry-related furan rings is indicated by the angle of their best planes of 0.00 (12)°. The alkynyl moieties shows a parallel orientation to the best plane of the furan moieties with an angle of 2.48 (19)°. The triple bond C8≡C9 is clearly characterized by the distance of 1.174 (3) Å. The packing diagram (Fig. 2) shows a linear intermolecular C9—H9⋯O2 contact with a H9⋯O2 distance of 2.39 Å between the alkynyl moiety and the ether function. A weak intermolecular C3—H3⋯O1 interaction with a H3⋯O1 distance of 2.87 Å between neighboring furan moieties along the direction of the *c* axis is observed.

Experimental

The compound was prepared by the reduction of 2-hydroxy-1,2-bis(5-methylfuran-2-yl)ethanone to the corresponding 1,2-diol and propargylation of the latter with propargyl bromide in the presence of a base as described in the literature (Hashmi, Wölfle *et al.*, 2007). The two diastereomers were separated by column chromatography on silica gel (PE—EtOAc—CH₂Cl₂, 30:1:2) as described there, the diastereomer eluting first crystallized by slow evaporation from a chloroform solution. ¹H NMR spectroscopic data of the pure diastereomer: ¹H NMR (300 MHz, CDCl₃): δ = 2.30 (d, J = 1.0 Hz, 6 H), 2.36 (t, J = 2.4 Hz, 2 H), 3.93 (dd, J = 15.9, 2.4 Hz, 2 H), 4.08 (dd, J = 15.9, 2.4 Hz, 2 H), 4.91 (s, 2 H), 5.95 (dq, J = 3.1, 1.0 Hz, 2 H), 6.33 (d, J = 3.1 Hz, 2 H).

Refinement

H atoms were located in difference Fourier map and refined with fixed individual displacement parameters [$U(H) = 1.2U_{eq}(C)$ or $U(H) = 1.5U_{eq}(C_{methyl})$] using a riding model with C—H ranging from 0.93 to 0.97 Å. In addition, the methyl group was allowed to rotate but not to tip.

Figures

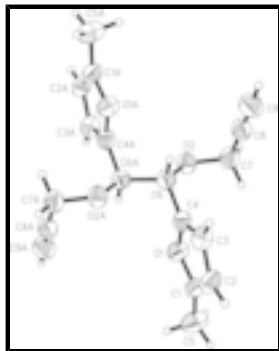


Fig. 1. The *ORTEP* drawing of (I) with atom numbering. Displacement ellipsoids are at the 50% probability level.

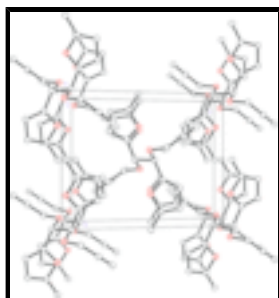


Fig. 2. Packing diagram (I) along the *a* axis.

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Crystal data

$C_{18}H_{18}O_4$

$M_r = 298.32$

Monoclinic, $P2_1/c$

Hall symbol: $-P\ 2ybc$

$a = 7.945\ (4)\ \text{\AA}$

$b = 9.215\ (5)\ \text{\AA}$

$c = 11.408\ (5)\ \text{\AA}$

$\beta = 107.17\ (4)^\circ$

$V = 798.1\ (7)\ \text{\AA}^3$

$Z = 2$

$F_{000} = 316$

$D_x = 1.241\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71073\ \text{\AA}$

Cell parameters from 26 reflections

$\theta = 16\text{--}18^\circ$

$\mu = 0.09\ \text{mm}^{-1}$

$T = 293\ (2)\ \text{K}$

Block, colourless

$0.9 \times 0.8 \times 0.5\ \text{mm}$

Data collection

Nicolet P3
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 293\ (2)\ \text{K}$

Wyckoff scan

Absorption correction: none

1506 measured reflections

$R_{\text{int}} = 0.048$

$\theta_{\text{max}} = 25.0^\circ$

$\theta_{\text{min}} = 2.7^\circ$

$h = 0 \rightarrow 9$

$k = 0 \rightarrow 10$

$l = -13 \rightarrow 12$

3 standard reflections

1402 independent reflections
 1204 reflections with $I > 2\sigma(I)$

every 50 reflections
 intensity decay: 3%

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.048$
 $wR(F^2) = 0.129$
 $S = 1.06$
 1402 reflections
 102 parameters
 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
 $w = 1/[\sigma^2(F_o^2) + (0.07P)^2 + 0.237P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.22 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.21 \text{ e } \text{\AA}^{-3}$
 Extinction correction: SHELXL97 (Sheldrick, 1997),
 $F_c^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
 Extinction coefficient: 0.019 (5)

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.83398 (16)	0.25136 (13)	0.46359 (11)	0.0466 (4)
C1	0.7962 (2)	0.1247 (2)	0.39765 (18)	0.0487 (5)
O2	0.78036 (15)	0.56861 (13)	0.46974 (11)	0.0456 (4)
C2	0.8173 (2)	0.1443 (2)	0.28653 (17)	0.0509 (5)
H2	0.8003	0.0751	0.2247	0.061*
C3	0.8704 (2)	0.2904 (2)	0.28085 (16)	0.0485 (5)
H3	0.8947	0.3353	0.2147	0.058*
C4	0.8788 (2)	0.35128 (19)	0.38888 (15)	0.0413 (4)
C5	0.7412 (3)	0.0006 (2)	0.4606 (2)	0.0710 (7)
H5A	0.7008	-0.0772	0.4032	0.107*
H5B	0.6476	0.0307	0.4925	0.107*
H5C	0.8395	-0.0319	0.5267	0.107*
C6	0.9246 (2)	0.49899 (18)	0.44007 (15)	0.0396 (4)
H6	0.9583	0.5583	0.3793	0.048*

supplementary materials

C7	0.6267 (2)	0.5851 (2)	0.36739 (17)	0.0502 (5)
H7A	0.5355	0.6319	0.3946	0.060*
H7B	0.5840	0.4897	0.3365	0.060*
C8	0.6578 (2)	0.6704 (2)	0.26747 (17)	0.0496 (5)
C9	0.6892 (3)	0.7371 (2)	0.1888 (2)	0.0602 (6)
H9	0.7140	0.7900	0.1264	0.072*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0517 (8)	0.0455 (7)	0.0437 (7)	-0.0066 (5)	0.0158 (6)	-0.0024 (5)
C1	0.0430 (10)	0.0440 (10)	0.0570 (11)	-0.0058 (8)	0.0117 (8)	-0.0089 (8)
O2	0.0399 (7)	0.0523 (8)	0.0448 (7)	0.0035 (5)	0.0126 (5)	-0.0032 (5)
C2	0.0436 (10)	0.0540 (11)	0.0542 (11)	-0.0057 (8)	0.0128 (8)	-0.0184 (9)
C3	0.0447 (10)	0.0607 (12)	0.0416 (9)	-0.0033 (8)	0.0151 (8)	-0.0047 (8)
C4	0.0368 (9)	0.0472 (10)	0.0398 (9)	-0.0017 (7)	0.0111 (7)	0.0016 (7)
C5	0.0828 (15)	0.0524 (12)	0.0795 (15)	-0.0167 (11)	0.0265 (12)	-0.0043 (11)
C6	0.0382 (9)	0.0420 (9)	0.0401 (9)	-0.0010 (7)	0.0139 (7)	0.0016 (7)
C7	0.0393 (9)	0.0547 (11)	0.0539 (11)	-0.0004 (8)	0.0099 (8)	-0.0017 (8)
C8	0.0455 (10)	0.0491 (10)	0.0497 (10)	0.0056 (8)	0.0071 (8)	-0.0033 (9)
C9	0.0651 (13)	0.0583 (12)	0.0547 (12)	0.0050 (10)	0.0139 (10)	0.0053 (10)

Geometric parameters (\AA , $^\circ$)

O1—C4	1.371 (2)	C5—H5A	0.9600
O1—C1	1.373 (2)	C5—H5B	0.9600
C1—C2	1.339 (3)	C5—H5C	0.9600
C1—C5	1.483 (3)	C6—C6 ⁱ	1.529 (3)
O2—C7	1.427 (2)	C6—H6	0.9800
O2—C6	1.438 (2)	C7—C8	1.464 (3)
C2—C3	1.418 (3)	C7—H7A	0.9700
C2—H2	0.9300	C7—H7B	0.9700
C3—C4	1.338 (2)	C8—C9	1.174 (3)
C3—H3	0.9300	C9—H9	0.9300
C4—C6	1.484 (2)		
C4—O1—C1	106.57 (14)	C1—C5—H5C	109.5
C2—C1—O1	109.62 (17)	H5A—C5—H5C	109.5
C2—C1—C5	134.38 (19)	H5B—C5—H5C	109.5
O1—C1—C5	115.99 (17)	O2—C6—C4	112.45 (14)
C7—O2—C6	113.80 (13)	O2—C6—C6 ⁱ	104.63 (16)
C1—C2—C3	107.06 (16)	C4—C6—C6 ⁱ	113.56 (17)
C1—C2—H2	126.5	O2—C6—H6	108.7
C3—C2—H2	126.5	C4—C6—H6	108.7
C4—C3—C2	106.91 (16)	C6 ⁱ —C6—H6	108.7
C4—C3—H3	126.5	O2—C7—C8	113.20 (15)
C2—C3—H3	126.5	O2—C7—H7A	108.9
C3—C4—O1	109.85 (16)	C8—C7—H7A	108.9
C3—C4—C6	133.41 (16)	O2—C7—H7B	108.9

O1—C4—C6	116.74 (14)	C8—C7—H7B	108.9
C1—C5—H5A	109.5	H7A—C7—H7B	107.8
C1—C5—H5B	109.5	C9—C8—C7	177.5 (2)
H5A—C5—H5B	109.5	C8—C9—H9	180.0
C4—O1—C1—C2	0.27 (19)	C1—O1—C4—C6	179.62 (14)
C4—O1—C1—C5	-179.11 (17)	C7—O2—C6—C4	-59.43 (18)
O1—C1—C2—C3	-0.2 (2)	C7—O2—C6—C6 ⁱ	176.88 (15)
C5—C1—C2—C3	179.0 (2)	C3—C4—C6—O2	118.0 (2)
C1—C2—C3—C4	0.1 (2)	O1—C4—C6—O2	-61.82 (19)
C2—C3—C4—O1	0.1 (2)	C3—C4—C6—C6 ⁱ	-123.5 (2)
C2—C3—C4—C6	-179.71 (18)	O1—C4—C6—C6 ⁱ	56.7 (2)
C1—O1—C4—C3	-0.22 (19)	C6—O2—C7—C8	-59.1 (2)

Symmetry codes: (i) $-x+2, -y+1, -z+1$.

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C9—H9 \cdots O2 ⁱⁱ	0.93	2.39	3.323 (3)	179
C3—H3 \cdots O1 ⁱⁱⁱ	0.93	2.87	3.566 (3)	132

Symmetry codes: (ii) $x, -y+3/2, z-1/2$; (iii) $x, -y+1/2, z-1/2$.

Fig. 1

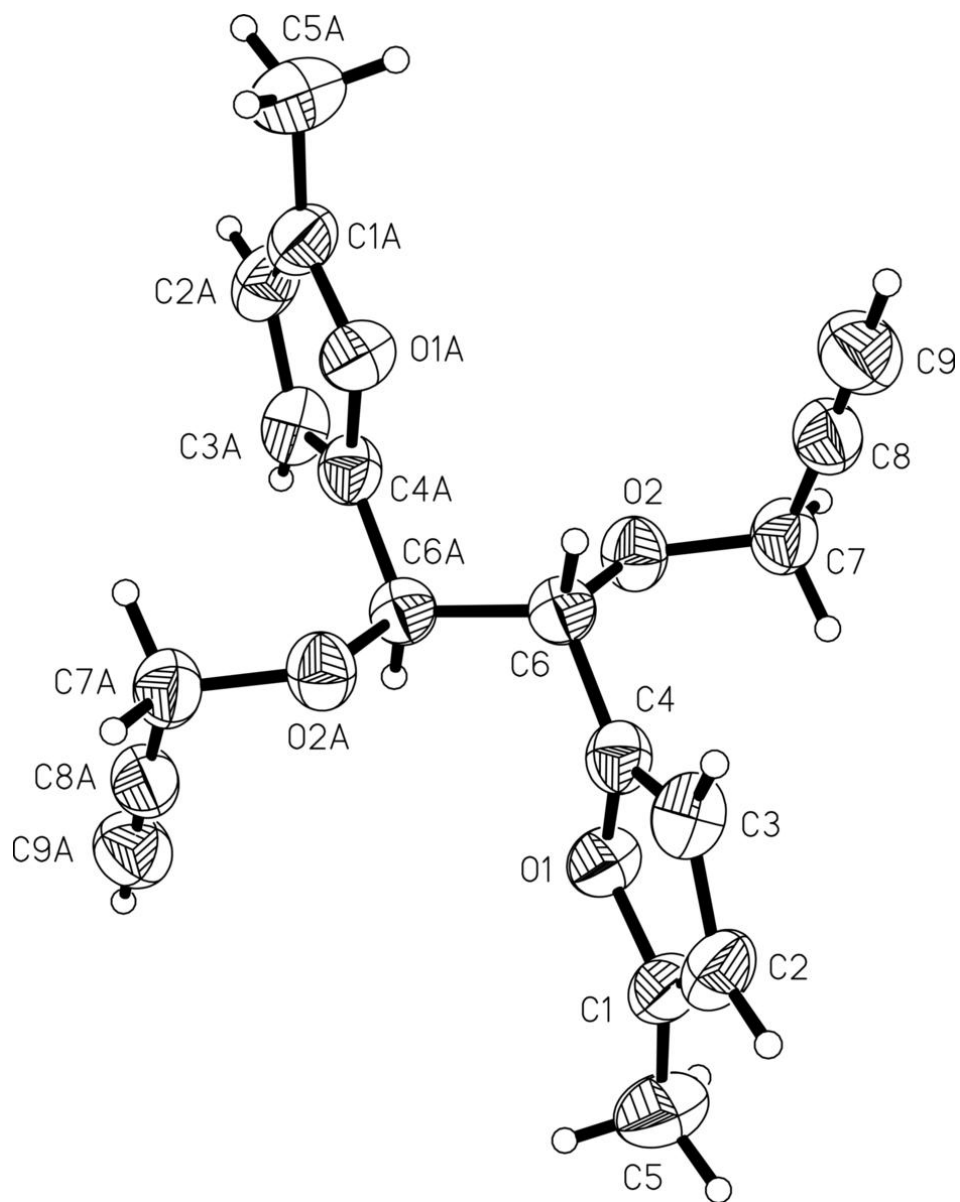


Fig. 2

