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Bis[5-(4-methoxybenzyl)furan-3-yl]-methanone

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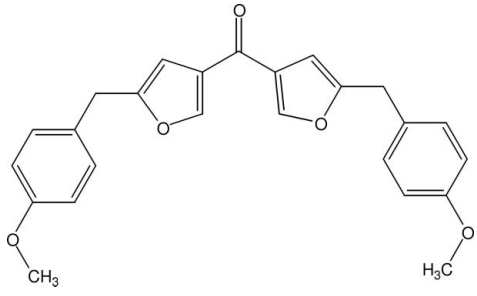
Key indicators: single-crystal X-ray study; T = 183 K; mean σ(C–C) = 0.006 Å; R factor = 0.081; wR factor = 0.195; data-to-parameter ratio = 13.4.

The title compound, $C_{25}H_{22}O_5$, was obtained by a dehydrogenative carbonylation reaction. It crystallizes with one half-molecule in the asymmetric unit. The molecules have crystallographic C_2 symmetry and the two atoms of the carbonyl group are located on the rotation axis. The methoxy groups are coplanar with the benzene ring to which they are attached [C—C—O—C = 1.0 (6)°]. The two furan rings are inclined at 17.3 (3)° with respect to each other and the dihedral angle between the furan ring and the benzene ring is 75.83 (12)°. The crystal structure is stabilized by C—H···O hydrogen bonds.

Related literature

The palladium-catalysed cycloisomerization of allenyl ketones delivers furan derivatives, see: Hashmi (1995); Hashmi & Schwarz (1997); Hashmi *et al.* (1999, 2000, 2004); Hashmi, Ruppert, Knöfel & Bats (1997).



Experimental

Crystal data

$C_{25}H_{22}O_5$
M_r = 402.43
Monoclinic, $C2/c$
a = 42.050 (2) Å
b = 5.9183 (2) Å
c = 8.3269 (3) Å
β = 99.594 (2)°
V = 2043.29 (14) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 183 K
0.60 × 0.30 × 0.05 mm

Data collection

Siemens CCD three-circle diffractometer
Absorption correction: none
8458 measured reflections
1854 independent reflections
1506 reflections with $I > 2\sigma(I)$
R_{int} = 0.045

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.081
$wR(F^2)$ = 0.195
S = 1.25
1854 reflections
138 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.31 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C14—H14···O32^{i}	0.95	2.23	3.114 (5)	154
C12—H12···O15^{ii}	0.95	2.87	3.782 (5)	163

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

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* (Sheldrick, 2008); software used to prepare material for publication: *PLATON* (Spek, 2009).

Palladium dichloride was donated by Umicore AG & Co KG.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: AT2869).

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supplementary materials

Acta Cryst. (2009). E**65**, o2325 [**doi:10.1107/S1600536809034333**]

Bis[5-(4-methoxybenzyl)furan-3-yl]methanone

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Comment

The palladium-catalysed cycloisomerization of allenyl ketones delivers furan derivatives (Hashmi, 1995; Hashmi & Schwarz, 1997; Hashmi *et al.*, 1999, 2000, 2004; Hashmi, Ruppert, Knöfel & Bats, 1997). In the context of these investigations, we also conducted the reaction of 1-(4-methoxy-phenyl)penta-3,4-dien-2-one in one atmosphere of carbon monoxide with 0.5 mol% of the $PdCl_2(MeCN)_2$ catalyst in acetonitrile. Besides starting material (7%), the monomeric cyclization product 2-(4-methoxybenzyl)furan (3%) and the cyclization/dimerization product (*E*)-1-[4-methoxybenzyl]-3-{5-[4-(methoxybenzyl]furan-3-yl}but-2-en-1-one (8%) as a new product type the title compound could be isolated (11%). The overall reaction to this new product type is a dehydrogenative carbonylation, mechanistic details are yet unknown.

The title compound crystallizes with half a molecule in the asymmetric unit. The molecules have crystallographic C_2 symmetry and the two atoms of the carbonyl group are located on the rotation axis. The methoxy groups are coplanar with the phenyl ring to which they are attached [C3—C4—O41—C42 1.0 (6)°]. The two furan rings are inclined by 17.3 (3)° with respect to each other and the dihedral angle between the furan ring and the phenyl ring is 75.83 (12)°. The crystal structure is stabilized by C—H···O hydrogen bonds.

Experimental

1.30 mmol (245 mg) of 1-(4-methoxy-phenyl)penta-3,4-dien-2-one were dissolved in 7.7 ml MeCN and degassed. The solution was stirred under one atmosphere of CO for two hours, then 6.6 µmol (1.7 mg) $Pd(MeCN)_2Cl_2$ in 0.3 ml MeCN were added. After stirring for 20 h at room temperature the solvent was removed *in vacuo* and the residue was purified by column chromatography on silica gel (eluting with hexanes/ethyl acetate, 5:1). Thus 11% (28.5 mg, 70.8 µmol) of the title compound were obtained. R_f (H/EE, 5:1) = 0.18. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 3.79 (s, 6 H), 3.91 (s, 4 H), 6.42 (d, *J* = 0.9 Hz, 2 H), 6.83- 6.88 (m, 4 H), 7.13–7.20 (m, 4 H), 7.84 (d, *J* = 0.9 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 33.37 (t, 2 C), 55.14 (q, 2 C), 105.62 (d, 2 C), 113.93 (d, 4 C), 128.16 (s, 2 C), 128.81 (s, 2 C), 129.63 (d, 4 C), 145.69 (d, 2 C), 156.96 (s, 2 C), 158.37 (s, 2 C), 189.94 (s).

Refinement

H atoms were located in a difference map but finally geometrically positioned and refined using a riding model with fixed individual displacement parameters [U_{iso}(H) = 1.2 U_{eq}(C) or U_{iso}(H) = 1.5 U_{eq}(C_{methyl})] and with $C_{aromatic}$—H= 0.95 Å, C_{methyl}—H = 0.98Å and $C_{methylene}$—H = 0.99 Å.

Figures

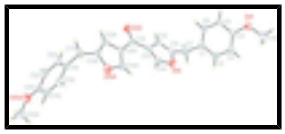


Fig. 1. Perspective view of the title compound with the atom numbering; displacement ellipsoids are at the 50% probability level. Symmetry operator for generating equivalent atoms: (A) 1 - *x*, *y*, 1/2 - *z*.

Bis[5-(4-methoxybenzyl)furan-3-yl]methanone

Crystal data

$C_{25}H_{22}O_5$	F_{000} = 848
M_r = 402.43	D_x = 1.308 Mg m^{-3}
Monoclinic, *C*2/*c*	Mo *K*α radiation, λ = 0.71073 Å
Hall symbol: -C 2yc	Cell parameters from 5761 reflections
a = 42.050 (2) Å	θ = 5.2–24.8º
b = 5.9183 (2) Å	μ = 0.09 mm^{-1}
c = 8.3269 (3) Å	*T* = 183 K
β = 99.594 (2)º	Plate, colourless
V = 2043.29 (14) Å^3	0.60 × 0.30 × 0.05 mm
Z = 4	

Data collection

Siemens CCD three-circle diffractometer	1506 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	R_{int} = 0.045
Monochromator: graphite	θ_{max} = 26.2º
T = 183 K	θ_{min} = 2.0º
ω scans	*h* = −50→51
Absorption correction: none	*k* = −7→7
8458 measured reflections	*l* = −10→9
1854 independent reflections	

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)]$ = 0.081	$w = 1/[\sigma^2(F_o^2) + (0.0374P)^2 + 9.4535P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.195	$(\Delta/\sigma)_{max} < 0.001$
S = 1.25	$\Delta\rho_{max}$ = 0.31 e Å^{-3}
1854 reflections	$\Delta\rho_{min}$ = −0.23 e Å^{-3}
138 parameters	Extinction correction: SHELXL97 (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Extinction coefficient: 0.0039 (8)

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 $F^2 > \sigma(F^2)$ 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}
C1	0.37264 (9)	0.2789 (7)	0.4374 (5)	0.0332 (9)
C2	0.35544 (9)	0.0841 (7)	0.4534 (5)	0.0385 (10)
H2	0.3643	−0.0267	0.5307	0.046*
C3	0.32526 (9)	0.0460 (7)	0.3586 (5)	0.0389 (10)
H3	0.3137	−0.0887	0.3716	0.047*
C4	0.31251 (9)	0.2064 (7)	0.2458 (5)	0.0328 (9)
O41	0.28319 (6)	0.1887 (5)	0.1431 (4)	0.0422 (8)
C42	0.26472 (10)	−0.0101 (9)	0.1577 (6)	0.0534 (13)
H42A	0.2618	−0.0290	0.2712	0.080*
H42B	0.2761	−0.1418	0.1237	0.080*
H42C	0.2436	0.0038	0.0881	0.080*
C5	0.32947 (9)	0.4037 (7)	0.2275 (5)	0.0363 (10)
H5	0.3207	0.5142	0.1499	0.044*
C6	0.35934 (9)	0.4378 (7)	0.3238 (5)	0.0364 (10)
H6	0.3709	0.5729	0.3114	0.044*
C7	0.40530 (9)	0.3207 (8)	0.5416 (5)	0.0415 (11)
H7A	0.4047	0.4680	0.5974	0.050*
H7B	0.4092	0.2022	0.6265	0.050*
C11	0.43293 (9)	0.3219 (7)	0.4488 (5)	0.0339 (9)
C12	0.45192 (8)	0.4804 (7)	0.4054 (4)	0.0308 (9)
H12	0.4509	0.6373	0.4279	0.037*
C13	0.47441 (8)	0.3727 (6)	0.3184 (5)	0.0297 (9)
C31	0.5000	0.4907 (9)	0.2500	0.0297 (12)
O32	0.5000	0.6987 (7)	0.2500	0.0418 (10)
C14	0.46659 (10)	0.1524 (7)	0.3128 (6)	0.0418 (11)
H14	0.4774	0.0387	0.2618	0.050*
O15	0.44090 (7)	0.1147 (5)	0.3907 (4)	0.0466 (9)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0262 (19)	0.044 (2)	0.032 (2)	0.0024 (17)	0.0115 (16)	−0.0021 (18)
C2	0.034 (2)	0.045 (3)	0.037 (2)	0.0054 (18)	0.0087 (18)	0.0062 (19)
C3	0.035 (2)	0.039 (2)	0.045 (2)	−0.0023 (18)	0.0119 (19)	0.005 (2)
C4	0.0239 (18)	0.041 (2)	0.035 (2)	0.0018 (16)	0.0100 (16)	−0.0027 (18)
O41	0.0297 (14)	0.0454 (18)	0.0502 (18)	−0.0019 (13)	0.0032 (13)	0.0012 (14)
C42	0.040 (2)	0.054 (3)	0.063 (3)	−0.014 (2)	−0.002 (2)	−0.003 (3)
C5	0.032 (2)	0.036 (2)	0.041 (2)	0.0020 (17)	0.0063 (18)	0.0038 (18)
C6	0.031 (2)	0.037 (2)	0.044 (2)	−0.0043 (17)	0.0144 (18)	−0.0009 (19)
C7	0.030 (2)	0.060 (3)	0.036 (2)	0.000 (2)	0.0095 (17)	−0.001 (2)
C11	0.0252 (19)	0.045 (2)	0.031 (2)	0.0035 (17)	0.0023 (16)	−0.0062 (18)
C12	0.0280 (19)	0.035 (2)	0.028 (2)	0.0045 (16)	0.0011 (16)	−0.0044 (17)
C13	0.0245 (18)	0.030 (2)	0.035 (2)	0.0011 (16)	0.0040 (15)	0.0000 (17)
C31	0.028 (3)	0.026 (3)	0.035 (3)	0.000	0.004 (2)	0.000
O32	0.040 (2)	0.031 (2)	0.055 (3)	0.000	0.012 (2)	0.000
C14	0.036 (2)	0.032 (2)	0.063 (3)	0.0020 (18)	0.023 (2)	−0.002 (2)
O15	0.0380 (16)	0.0336 (17)	0.074 (2)	−0.0051 (13)	0.0252 (15)	−0.0007 (15)

Geometric parameters (Å, °)

C1—C2	1.380 (6)	C6—H6	0.9500
C1—C6	1.384 (6)	C7—C11	1.498 (5)
C1—C7	1.518 (5)	C7—H7A	0.9900
C2—C3	1.397 (6)	C7—H7B	0.9900
C2—H2	0.9500	C11—C12	1.321 (6)
C3—C4	1.380 (6)	C11—O15	1.380 (5)
C3—H3	0.9500	C12—C13	1.433 (5)
C4—O41	1.383 (5)	C12—H12	0.9500
C4—C5	1.390 (6)	C13—C14	1.344 (6)
O41—C42	1.426 (5)	C13—C31	1.474 (4)
C42—H42A	0.9800	C31—O32	1.231 (7)
C42—H42B	0.9800	C31—C13^{i}	1.474 (4)
C42—H42C	0.9800	C14—O15	1.368 (5)
C5—C6	1.388 (5)	C14—H14	0.9500
C5—H5	0.9500		
C2—C1—C6	118.4 (4)	C5—C6—H6	119.3
C2—C1—C7	121.3 (4)	C11—C7—C1	114.3 (3)
C6—C1—C7	120.3 (4)	C11—C7—H7A	108.7
C1—C2—C3	121.5 (4)	C1—C7—H7A	108.7
C1—C2—H2	119.3	C11—C7—H7B	108.7
C3—C2—H2	119.3	C1—C7—H7B	108.7
C4—C3—C2	119.1 (4)	H7A—C7—H7B	107.6
C4—C3—H3	120.4	C12—C11—O15	110.0 (3)
C2—C3—H3	120.4	C12—C11—C7	134.5 (4)
C3—C4—O41	125.1 (4)	O15—C11—C7	115.5 (4)

C3—C4—C5	120.3 (4)	C11—C12—C13	107.6 (4)
O41—C4—C5	114.6 (4)	C11—C12—H12	126.2
C4—O41—C42	116.9 (3)	C13—C12—H12	126.2
O41—C42—H42A	109.5	C14—C13—C12	105.7 (3)
O41—C42—H42B	109.5	C14—C13—C31	129.5 (4)
H42A—C42—H42B	109.5	C12—C13—C31	124.8 (4)
O41—C42—H42C	109.5	O32—C31—C13^{i}	118.3 (2)
H42A—C42—H42C	109.5	O32—C31—C13	118.3 (2)
H42B—C42—H42C	109.5	C13^{i}—C31—C13	123.4 (5)
C6—C5—C4	119.4 (4)	C13—C14—O15	110.5 (3)
C6—C5—H5	120.3	C13—C14—H14	124.8
C4—C5—H5	120.3	O15—C14—H14	124.8
C1—C6—C5	121.3 (4)	C14—O15—C11	106.2 (3)
C1—C6—H6	119.3		
C6—C1—C2—C3	−0.2 (6)	C1—C7—C11—O15	−70.6 (5)
C7—C1—C2—C3	179.5 (4)	O15—C11—C12—C13	−1.9 (4)
C1—C2—C3—C4	0.4 (6)	C7—C11—C12—C13	179.3 (4)
C2—C3—C4—O41	179.1 (4)	C11—C12—C13—C14	1.3 (5)
C2—C3—C4—C5	−0.3 (6)	C11—C12—C13—C31	−179.5 (3)
C3—C4—O41—C42	1.0 (6)	C14—C13—C31—O32	170.0 (4)
C5—C4—O41—C42	−179.6 (4)	C12—C13—C31—O32	−9.0 (4)
C3—C4—C5—C6	0.0 (6)	C14—C13—C31—C13^{i}	−10.0 (4)
O41—C4—C5—C6	−179.4 (3)	C12—C13—C31—C13^{i}	171.0 (4)
C2—C1—C6—C5	−0.1 (6)	C12—C13—C14—O15	−0.2 (5)
C7—C1—C6—C5	−179.8 (4)	C31—C13—C14—O15	−179.3 (3)
C4—C5—C6—C1	0.2 (6)	C13—C14—O15—C11	−0.9 (5)
C2—C1—C7—C11	113.0 (4)	C12—C11—O15—C14	1.8 (5)
C6—C1—C7—C11	−67.3 (5)	C7—C11—O15—C14	−179.2 (3)
C1—C7—C11—C12	108.1 (5)		

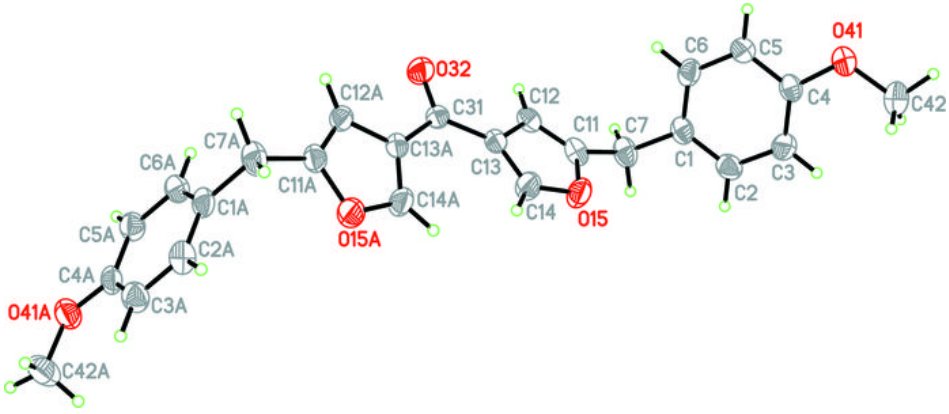
Symmetry codes: (i) −*x*+1, *y*, −*z*+1/2.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C14—H14···O32^{ii}	0.95	2.23	3.114 (5)	154
C12—H12···O15^{iii}	0.95	2.87	3.782 (5)	163

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

Fig. 1


041
C6
C5
C4
C42
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C12A
C31
C12
C11
C7
C1
C2
C3
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C6A
C13A
C13
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C14A
C14
015
C1A
C5A
C2A
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C4A
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C42A