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3,3-Bis(2-furylmethyl)-2-methyl-4-oxocyclohex-1-ene-1-carboxylic acid

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In the title molecule, $C_{18}H_{18}O_5$, the cyclohexene ring adopts an envelope conformation. The dihedral angle between the two furan rings is 65.9 (1)°. In the crystal structure, the carboxyl groups of inversion-related moleules are involved in the formation of dimers through O—H···O hydrogen bonds.

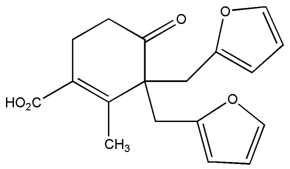
Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.002 Å
R factor = 0.048
wR factor = 0.139
Data-to-parameter ratio = 18.1

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

The title compound, (I), is a novel bisalkylation product of Hagemann's ester. Many natural and non-natural products involve spiro junctions. Recently, we obtained (I) as a by-product in the alkylation of Hagemann's ester with ^{t}BuOK/^{t}BuOH/2-furylmethyl chloride (Chakraborty *et al.*, 1997). We report here the crystal and molecular structure of (I).



(I)

The title molecule contains one cyclohexene ring (C1—C6) and two furan rings (C8—C11/O1 and C13—C16/O2; Fig. 1). The dihedral angle between the two furan rings is 65.9 (1)°. The cyclohexene ring adopts an envelope conformation, with atom C5 deviating from the mean plane passing through the remaining atoms in that ring by 0.670 (3) Å. The plane of the carboxyl group is twisted from the C1—C4/C6 plane by 14.1 (3)°. The C2—C3 distance of 1.346 (2) Å confirms the double-bond character of this linkage. The molecular structure is stabilized by C—H···O interactions (Table 2) involving the carbonyl O atoms. As usual, the carboxyl group serves, simultaneously, as hydrogen-bond donor and acceptor, to form dimers through a centrosymmetric pair of O—H···O hydrogen bonds (Table 2 and Fig. 2). The geometry of this hydrogen bond agrees well with those reported by Jeffrey & Saenger (1994).

Experimental

Hagemann's ester, on reaction with ^{t}BuOK in ^{t}BuOH, followed by refluxing with 2-furylmethyl chloride, afforded the monoalkylated Hagemann's ester along with the bisalkylated product (Chakraborty *et al.*, 1997). The crude reaction mixture, on subsequent hydrolysis with KOH/EtOH–H_2O, furnished 2-(2-furylmethyl)-3-methylcyclohex-2-en-1-one and the title compound. Single crystals of the latter were grown by slow evaporation of an ethyl acetate solution of the title compound [m.p.: 415–416 K ($CH_3COOCH_2CH_3$)]. IR spectroscopy (KBr, cm^{-1}): 3140, 1718, 1684; ^{1}H NMR (200 MHz, $CDCl_3$): δ (p.p.m.) 2.00–2.16 (*m*, 4 H), 2.26 (*s*, 3 H), 2.98 (*d*, 2 H, J = 14.5 Hz), 3.33(*d*, 2 H, J = 14.5 Hz), 5.93(*d*, 2 H, J = 3.25 Hz), 6.20 (*dd*, 2 H, J =

3.25 and 1.9 Hz), 7.23 (*d*, 2 H, *J* = 1.9 Hz); ^{13}C NMR (50 MHz, CDCl$_3$): δ (p.p.m.) 16.72, 23.53, 35.60, 38.06, 58.29, 107.79, 110.27, 127.61, 141.66, 148.80, 150.79, 172.99, 211.88; MS (*m*/*z*): 314 (M$^+$), 233, 148, 81 (base peak), 53.

Crystal data

$C_{18}H_{18}O_5$
M_r = 314.32
Monoclinic, $P2_1/n$
a = 7.125 (1) Å
b = 8.798 (1) Å
c = 25.625 (2) Å
β = 91.214 (1)°
V = 1606.0 (3) Å^3
Z = 4

D_x = 1.300 Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 5554 reflections
θ = 2.0–28.0°
μ = 0.10 mm^{-1}
T = 298 (2) K
Block, colourless
0.55 × 0.55 × 0.55 mm

Data collection

Bruker SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.866, T_{max} = 0.950
9924 measured reflections

3824 independent reflections
3057 reflections with $I > 2\sigma(I)$
R_{int} = 0.020
θ_{max} = 28.3°
h = −9 → 9
k = −7 → 11
l = −34 → 34

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.048
$wR(F^2)$ = 0.139
S = 1.06
3824 reflections
211 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0606P)^2 + 0.5648P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ < 0.001
$\Delta\rho_{max}$ = 0.44 e Å^{-3}
$\Delta\rho_{min}$ = −0.29 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.036 (3)

Table 1
Selected geometric parameters (Å, °).

O3—C18	1.216 (2)	C8—C9	1.343 (2)
O4—C18	1.299 (2)	C10—C11	1.320 (3)
O5—C6	1.212 (2)	C13—C14	1.345 (3)
C2—C3	1.346 (2)	C15—C16	1.316 (3)
C2—C3—C18—O3	11.8 (3)	C2—C3—C18—O4	−167.8 (2)
C4—C3—C18—O3	−172.2 (2)	C4—C3—C18—O4	8.2 (2)

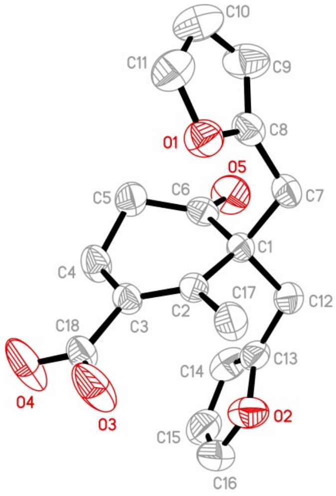


Figure 1
A view of the title molecule showing 50% probability displacement ellipsoids and the atomic numbering scheme. H atoms have been omitted for clarity.

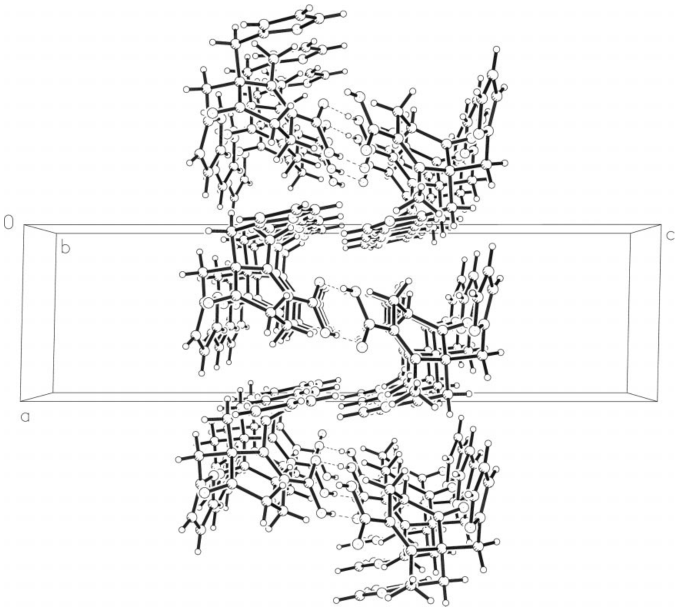


Figure 2
Part of the molecular packing, showing the dimer formation.

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O4—H4···O3^{i}	0.82	1.83	2.649 (2)	176
C12—H12A···O5	0.97	2.47	2.828 (2)	101
C17—H17C···O3	0.96	2.40	2.777 (2)	103

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

All the H atoms were positioned geometrically and allowed to ride on the parent atoms, with aromatic C—H = 0.93 Å, methylene C—H = 0.97 Å, methyl C—H = 0.96 Å and O—H = 0.82 Å. The U_{iso}(H) values were set at 1.5U_{eq}(C) for the methyl H atoms and at 1.2U_{eq}(C) for other C-bound H atoms; U_{iso}(H) for the carboxyl H atom was set equal to 1.5U_{eq}(O). A rotating group model was used for the methyl group. Owing to the large fraction of weak data at higher angles, the completeness is slightly low (96%).

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

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