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Key indicators

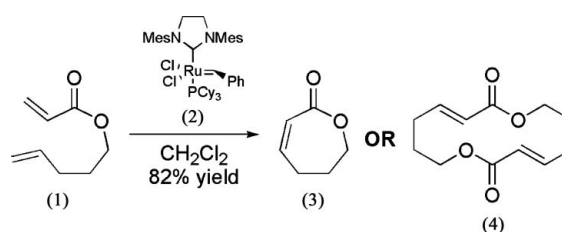
Single-crystal X-ray study
 $T = 301\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.002\text{ \AA}$
 R factor = 0.042
 wR factor = 0.123
Data-to-parameter ratio = 17.6For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.**(*E,E*)-1,8-Dioxacyclotetradeca-3,10-diene-
2,9-dione**

The title compound, $\text{C}_{12}\text{H}_{16}\text{O}_4$, has an unconventional weak hydrogen-bonding pattern. A network of weak intermolecular hydrogen bonds between an alkane group and the carbonyl groups stabilizes the molecular packing. The asymmetric unit contains one half-molecule and the complete molecule is generated by an inversion center.

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Comment

Compound (4) has been cited several times in the literature (Fürstner *et al.*, 2000; Le Floc'h *et al.*, 1991; Yvergnaux *et al.*, 1989). We have developed the synthesis of (4) and report here its crystal structure for the first time (Fig. 1).



Given the expected similarity between the NMR spectra of (4) and potential product (3), we wished to determine unequivocally which compound we had synthesized (Chatterjee *et al.*, 2000; Le Floc'h *et al.*, 1991; Moriarty *et al.*, 1990). Therefore, we grew crystals suitable for single-crystal X-ray analysis. Previous reports of this compound described it as an oil; however (4) produced suitable crystals with a melting point of 353.5 K.

There are no conventional strong hydrogen bonds in the structure owing to the lack of a traditional hydrogen-bond donor. A C—H···O hydrogen bond is identified (Table 1). This bond is considered to be moderate to strong for a C—H···O bond (Desiraju, 1996). The donating proton approaches the lone pair of the carbonyl (Fig. 2).

Generally, hydrogen-donor strength for CH groups depends on the acid strength of the group, which varies with carbon hybridization, $sp^2 > sp^3$ (Steiner, 2003). However, for compound (4), the alkane H atom donates, forming a weak hydrogen bond to the carbonyl O atom, while the alkene H atom is not involved in hydrogen bonding. This emphasizes the fact that solid-state activity depends on both electronic and steric factors (Desiraju, 1996).

A similar 20-membered ring compound [Cambridge Structural Database; Version 1.7 (Allen, 2002) refcode JECSEP (Yvergnaux *et al.*, 1989)] shows similar weak C—H···O hydrogen bonds. Unlike compound (4), JECSEP has both sp^2 and sp^3 donors in hydrogen bonding. Both JECSEP and compound (4) adopt a rectangular-like ring conformation.

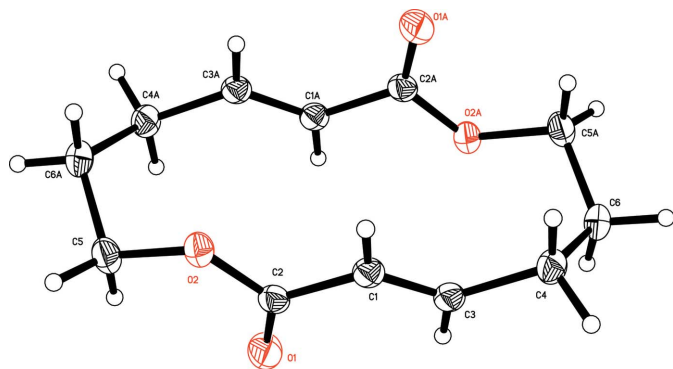


Figure 1
View of the molecular structure of (4), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 20% probability level. H atoms are represented by circles of arbitrary size. [Symmetry code: (A) $-x + 2, -y + 1, -z$.]

Experimental

Compound (1) (0.25 mmol) was added *via* a syringe to a stirred solution of (2) (5 mol%) in CH_2Cl_2 . The flask was fitted with a condenser and the mixture refluxed under nitrogen for 12 h. The reaction mixture was then reduced to a volume of 0.5 ml and purified on a silica-gel column, eluting with hexane–ethyl acetate (9:1 *v/v*) ($R_F = 1/4$). A clear oil was obtained (Chatterjee *et al.*, 2000). A sample of (4) was grown by dissolving the chromatographed syrup in heptane at a concentration of approximately 50 mg ml^{-1} and allowing the solvent to evaporate slowly overnight. A crystalline sample of (4) was removed from the flask and mounted on a glass fiber for data collection.

Crystal data

$\text{C}_{12}\text{H}_{16}\text{O}_4$	$Z = 1$
$M_r = 224.25$	$D_x = 1.272 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 6.442$ (3) Å	Cell parameters from 938 reflections
$b = 6.665$ (3) Å	$\theta = 28.3\text{--}0.9^\circ$
$c = 7.757$ (4) Å	$\mu = 0.10 \text{ mm}^{-1}$
$\alpha = 72.037$ (7)°	$T = 301$ (2) K
$\beta = 77.661$ (8)°	Plate, colorless
$\gamma = 68.409$ (7)°	$0.51 \times 0.41 \times 0.17 \text{ mm}$
$V = 292.7$ (2) Å ³	

Data collection

Bruker SMART CCD area-detector diffractometer	1440 independent reflections
φ and ω scans	1278 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 2002)	$R_{\text{int}} = 0.020$
$T_{\text{min}} = 0.754, T_{\text{max}} = 0.984$	$\theta_{\text{max}} = 28.3^\circ$
5226 measured reflections	$h = -8 \rightarrow 8$
	$k = -8 \rightarrow 8$
	$l = -10 \rightarrow 10$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0712P)^2 + 0.031P]$
$R[F^2 > 2\sigma(F^2)] = 0.042$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.123$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.05$	$\Delta\rho_{\text{max}} = 0.20 \text{ e \AA}^{-3}$
1440 reflections	$\Delta\rho_{\text{min}} = -0.16 \text{ e \AA}^{-3}$
82 parameters	Extinction correction: SHELXL97
H atoms treated by a mixture of independent and constrained refinement	Extinction coefficient: 0.17 (3)

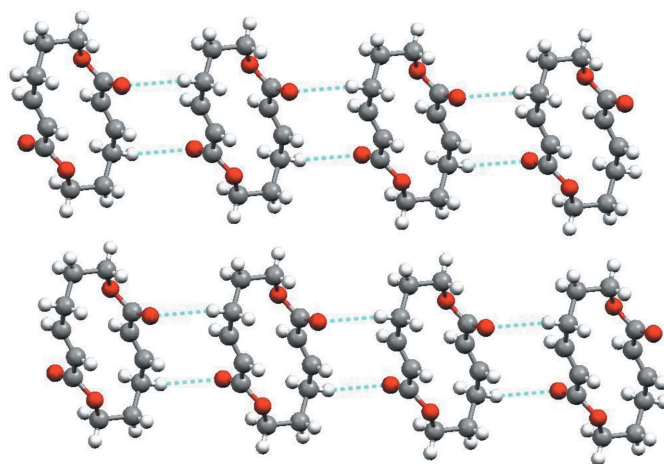


Figure 2
The intermolecular hydrogen bonding of (4), shown as dashed lines.

Table 1

Hydrogen-bond geometry (Å, °).

$D\text{--}H\cdots A$	$D\text{--}H$	$H\cdots A$	$D\cdots A$	$D\text{--}H\cdots A$
$\text{C4--H4A}\cdots\text{O1}^i$	0.97	2.67	3.544 (2)	150

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

Alkene H atoms were located in a difference Fourier map and their positions were refined freely with isotropic displacement parameters. The remaining H atoms were placed in idealized locations ($\text{C--H} = 0.97 \text{ \AA}$) and refined with riding constraints, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: SMART (Bruker, 2003); cell refinement: SMART; data reduction: SAINT-Plus (Bruker, 2003); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 2003); software used to prepare material for publication: SHELXTL.

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