(5RS,6RS)-5,6-Di-*tert*-butyl-2,2,9,9-tetramethyldecane-3,8-dione

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The title compound, $C_{22}H_{42}O_2$, displays approximate twofold symmetry. The elongated central single bond [1.563 (3) Å] and widened angles [116.00 (16) and 115.80 (16)°] at the methylene C atoms are probably indicators of steric strain. Molecules are linked in inversion-symmetric pairs by a bifurcated weak hydrogen-bond system of the form $(C-H)_2\cdots O$.

Comment

Subjecting 2,2,6,6-tetramethylhept-4-en-3-one, (1), to the conditions of the McMurry coupling (Lenoir, 1977) causes a dimerization, but surprisingly this affects not the carbonyl group of the substrate but its C=C double bond. As shown here by X-ray structural analysis, the dimer obtained in excellent yield (80–90%) is the diketone 5,6-di-*tert*-butyl-2,2,9,9-tetramethyldecane-3,8-dione, (2).
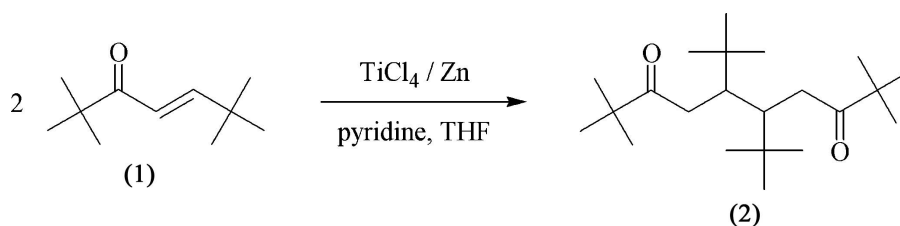

The molecule of (2) is shown in Fig. 1. Of the two possible diastereomeric products, the 5RS,6RS isomer was formed rather than the *meso* isomer, for reasons that remain to be investigated. The bond lengths and torsion angles along the chain C1–C10 reflect the approximate twofold symmetry of the molecule (Table 1). The elongated single bond C5—C6 and the widened sp^3 angles C3—C4—C5 and C6—C7—C8 may indicate steric strain.

The molecules are linked in inversion-symmetric pairs by the weak, bifurcated hydrogen bonds given in Table 2.

Experimental

To a suspension of zinc dust (0.45 g, 6.8 mmol) and TiCl$_4$ (0.35 ml, 0.61 g, 3.2 mmol) in anhydrous THF (10 ml) and pyridine (0.2 ml) was added a solution of (1) (0.5 g, 2.97 mmol) in anhydrous THF (5 ml). After stirring for 18 h at room temperature, the mixture was worked-up and the resulting crystalline raw product purified by sublimation. The spectroscopic data of the analytically pure product (0.42 g, 84%; unpublished results) agreed with the proposed structure.
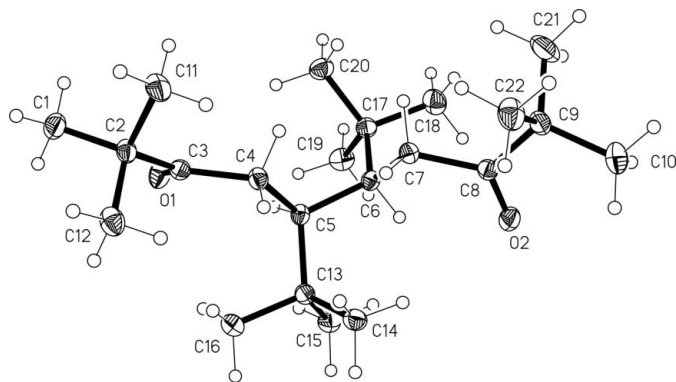
Figure 1
The molecular structure of the title compound in the crystal structure. Displacement ellipsoids are drawn at the 30% probability level.

Crystal data

$C_{22}H_{42}O_2$
$M_r = 338.56$
Monoclinic, $P2_1/c$
$a = 12.353 (3)$ Å
$b = 17.289 (4)$ Å
$c = 11.475 (3)$ Å
$\beta = 117.46 (2)°$
$V = 2174.7 (9)$ Å^3
$Z = 4$

$D_x = 1.034$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 60 reflections
$\theta = 10–11°$
$\mu = 0.06$ mm^{-1}
$T = 143 (2)$ K
Tablet, colourless
$0.7 \times 0.4 \times 0.25$ mm

Data collection

Stoe Stadi-4 diffractometer
ω/θ scans
Absorption correction: none
4032 measured reflections
3827 independent reflections
2762 reflections with $I > 2\sigma(I)$
$R_{int} = 0.017$

$\theta_{max} = 25.0°$
$h = -14 \rightarrow 13$
$k = 0 \rightarrow 20$
$l = 0 \rightarrow 13$
3 standard reflections
    frequency: 60 min
    intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.052$
$wR(F^2) = 0.127$
$S = 1.03$
3827 reflections
229 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0441P)^2 + 0.9108P]$
    where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.18$ e Å^{-3}
$\Delta\rho_{min} = -0.18$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C2—C3	1.535 (3)	C6—C7	1.549 (3)
C3—C4	1.519 (3)	C7—C8	1.517 (3)
C4—C5	1.546 (3)	C8—C9	1.539 (3)
C5—C6	1.563 (3)		
C3—C4—C5	116.00 (16)	C8—C7—C6	115.80 (16)
C1—C2—C3—C4	166.07 (17)	C5—C6—C7—C8	135.27 (17)
C2—C3—C4—C5	163.84 (17)	C6—C7—C8—C9	159.66 (16)
C3—C4—C5—C6	139.11 (17)	C7—C8—C9—C10	169.88 (17)
C4—C5—C6—C7	36.0 (2)		

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C15—H15$A\cdots$O2^i	0.98	2.53	3.333 (3)	140
C19—H19$B\cdots$O2^i	0.98	2.58	3.561 (3)	175

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

Methyl H atoms were located in difference syntheses, idealized (C—H = 0.98Å and H—C—H = 109.5°) and refined on the basis of rigid groups allowed to rotate but not tip. Methylene and methine H atoms were placed in calculated opositions (C—H = 0.99 and 1.00Å, respectively) and allowed to ride on their parent C atom. U_{iso}(H) values were fixed at 1.2 times U_{eq} of the parent atom.

Data collection: *DIF4* (Stoe, 1992); cell refinement: *DIF4*; data reduction: *REDU4* (Stoe, 1992); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1994); software used to prepare material for publication: *SHELXL97*.

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