

Precursors to dodecahedrane

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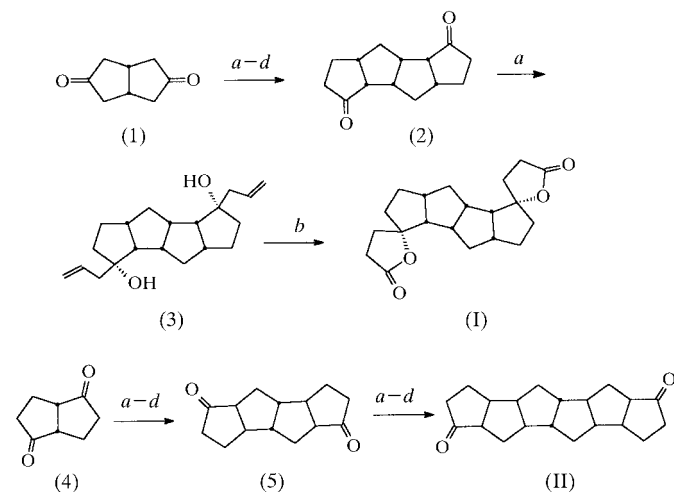
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The title compounds, (2*R*,2''*S*,3*b*'*S*,4*a*'*R*,7*b*'*S*,8*a*'*R*)-perhydrodispiro[furan-2,3'-dicyclopenta[*a,e*]pentalene-7',2''-furan]-5,5''-dione, C₂₀H₂₆O₄, and (3*aR*,3*bR*,4*aR*,4*bS*,5*aS*,8*aR*,8*bR*,9*aR*,9*bS*,10*aS*)-perhydrodipentaleno[2,1-*a*:2',1'-*e*]pentalene-1,6-dione, C₂₀H₂₆O₂, are intermediates identified during the synthesis of dodecahedrane. Crystallographic studies have established the ring-junction stereochemistry for these important intermediates. All the ring junctions are *cis*-fused, and the molecular packing is stabilized by van der Waals interactions.

Comment

The symmetrical nature of dodecahedrane offers many routes for its synthesis, and there are several ways in which the



- (a) Allyl bromide, Mg-ether/THF; (b) NaBH₄, BF₃·Et₂O, THF; Jones
(c) Methanesulphonic acid, P₂O₅; (d) 10% Pd/C, EtOAc, 304 kPa

cyclopentane rings can be assembled (Ternansky *et al.*, 1982; Fessener *et al.*, 1987). However, the strategy developed should

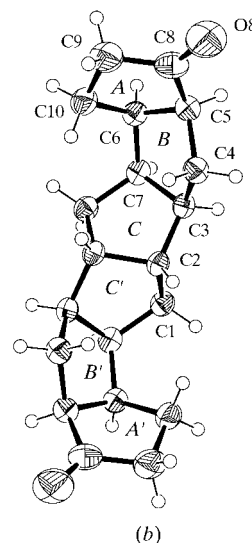
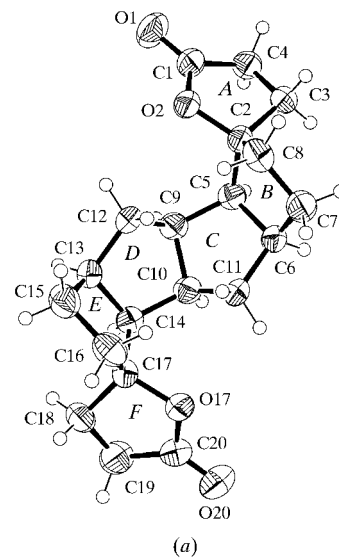


Figure 1

A view of the molecular structures of (a) (I) and (b) (II), showing displacement ellipsoids at the 50% probability level and the atomic numbering schemes.

involve the fusion of cyclopentane rings with the desired *cis* stereochemistry. A simple methodology for cyclopentane annulation has been developed in order to acquire different (C₂)–C₂₀¹ hexaquinanes that are suitable precursors to dodecahedrane (Kotha *et al.*, 1997; Kotha *et al.*, 2002). Although the intermediates can be characterized on the basis of NMR spectral data, the stereochemistry at the ring junctions was ascertained only on the basis of X-ray diffraction analysis.

The structures of the title compounds, (I) and (II), are shown in Fig. 1. The ring junctions are *cis*-fused and the molecules have an 'opened out' conformation. A structure related to (II), reported by McKerverey *et al.* (1981), also exhibits a *cis*-fused ring junction, and all the H atoms at the ring junctions point in the same direction. However, in (II),

¹(C₂)–C₂₀ means twofold symmetry in a molecule of 20 atoms.

the H atoms at ring junction *C/C'* are oriented in the opposite direction to all other ring-junction H atoms.

Puckering parameters (Cremer & Pople, 1975) were calculated using *PARST97* (Nardelli, 1995). Five-membered rings *A*, *B*, *C*, *D* and *E* in (I) adopt envelope conformations, but the terminal five-membered ring, *i.e.* *F* (O17/C17–C18), exhibits a twisted-envelope conformation (Fig. 1 and Table 1). In (II), half of the molecule is present in the asymmetric unit, and rings *A* and *B* are in a twisted-envelope conformation (Table 3). In (I), atoms O1 and O20 lie in the planes through the five-membered rings to which they are attached, *i.e.* rings *A* and *F* (Fig. 1). However, in (II), atom O8 deviates significantly [0.169 (2) Å] from the plane of ring *A*.

Ring fusion may cause significant variations from the tetrahedral values for the exocyclic C–C–C bond angles centred at atoms C10, C14, C5, C9, C13 and C6 [121.2 (2), 120.5 (2), 120.3 (2), 121.6 (2), 115.3 (2) and 115.2 (2)°, respectively]. Similarly, in (II), the exocyclic bond angles centred at atoms C2, C3, C5, C6 and C7 [115.6 (1), 114.6 (1), 113.0 (1), 117.1 (1) and 117.8 (1)°, respectively] differ from the expected tetrahedral values. The packing of (I) is stabilized by weak C–H...O hydrogen bonds (Table 2), while the packing of (II) is stabilized by van der Waals interactions only.

Experimental

X-ray analysis of intermediate (I) established the required all-*cis-syn* stereochemistry at the ring junctions. The key tetracyclic dione, (2), obtained from (1) was converted to diol (3) by the Grignard addition reaction. Then (3) was converted to (I) *via* hydroboration followed by the Jones oxidation sequence. Similarly, hexacyclic ketone (II) was prepared from bicyclic dione (4) *via* intermediate (5). The proton-decoupled ¹³C NMR spectrum of (II) showed ten lines, as expected, which could be attributed to the presence of *C*₂ symmetry in the molecule. However, the spectral data did not allow us to assign the relative stereochemistry at the ring junctions. Crystallization of (II) afforded a single crystal suitable for X-ray analysis. The fusion at the ring junctions was unequivocally ascertained by X-ray diffraction studies.

Compound (I)

Crystal data

$C_{20}H_{26}O_4$	$D_x = 1.312 \text{ Mg m}^{-3}$
$M_r = 330.41$	Cu $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 25 reflections
$a = 7.085 (3) \text{ \AA}$	$\theta = 8.6\text{--}25.6^\circ$
$b = 12.064 (5) \text{ \AA}$	$\mu = 0.73 \text{ mm}^{-1}$
$c = 19.583 (5) \text{ \AA}$	$T = 293 (2) \text{ K}$
$\beta = 91.54 (3)^\circ$	Rectangular needle, colourless
$V = 1673.2 (11) \text{ \AA}^3$	$0.20 \times 0.05 \times 0.01 \text{ mm}$
$Z = 4$	

Data collection

Enraf–Nonius CAD-4 diffractometer	$\theta_{\text{max}} = 68.0^\circ$
Non-profiled $\omega/2\theta$ scans	$h = 0 \rightarrow 8$
3346 measured reflections	$k = 0 \rightarrow 14$
3054 independent reflections	$l = -23 \rightarrow 23$
1727 reflections with $I > 2\sigma(I)$	3 standard reflections
$R_{\text{int}} = 0.035$	frequency: 120 min
	intensity decay: none

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0676P)^2 + 0.0257P]$
$R[F^2 > 2\sigma(F^2)] = 0.051$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.143$	$(\Delta/\sigma)_{\text{max}} = 0.005$
$S = 1.02$	$\Delta\rho_{\text{max}} = 0.19 \text{ e \AA}^{-3}$
3054 reflections	$\Delta\rho_{\text{min}} = -0.26 \text{ e \AA}^{-3}$
217 parameters	
H-atom parameters constrained	

Table 1

Cremer & Pople (1975) conformational parameters for the rings in (I).

Ring	q_2 (Å)	Conformation
<i>A</i>	0.284 (3)	Envelope
<i>B</i>	0.400 (3)	Envelope
<i>C</i>	0.402 (3)	Envelope
<i>D</i>	0.411 (3)	Envelope
<i>E</i>	0.409 (3)	Envelope
<i>F</i>	0.257 (3)	Twist-envelope

Table 2

Hydrogen-bonding geometry (Å, °) for (I).

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
C4–H4B...O20 ⁱ	0.97	2.47	3.366 (4)	154
C19–H19B...O1 ⁱⁱ	0.97	2.39	3.314 (4)	159

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

Compound (II)

Crystal data

$C_{20}H_{26}O_2$	$D_x = 1.280 \text{ Mg m}^{-3}$
$M_r = 298.41$	Cu $K\alpha$ radiation
Monoclinic, $I2/a$	Cell parameters from 25 reflections
$a = 9.415 (8) \text{ \AA}$	$\theta = 22.1\text{--}28.6^\circ$
$b = 10.739 (2) \text{ \AA}$	$\mu = 0.63 \text{ mm}^{-1}$
$c = 15.332 (3) \text{ \AA}$	$T = 293 (2) \text{ K}$
$\beta = 92.58 (4)^\circ$	Rectangular block, colourless
$V = 1548.6 (14) \text{ \AA}^3$	$0.33 \times 0.20 \times 0.10 \text{ mm}$
$Z = 4$	

Data collection

Enraf–Nonius CAD-4 diffractometer	$\theta_{\text{max}} = 71.9^\circ$
Non-profiled $\omega/2\theta$ scans	$h = -1 \rightarrow 11$
1724 measured reflections	$k = 0 \rightarrow 13$
1505 independent reflections	$l = -18 \rightarrow 18$
1244 reflections with $I > 2\sigma(I)$	3 standard reflections
$R_{\text{int}} = 0.036$	frequency: 120 min
	intensity decay: none

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0437P)^2 + 1.1616P]$
$R[F^2 > 2\sigma(F^2)] = 0.040$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.109$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.06$	$\Delta\rho_{\text{max}} = 0.20 \text{ e \AA}^{-3}$
1505 reflections	$\Delta\rho_{\text{min}} = -0.17 \text{ e \AA}^{-3}$
100 parameters	
H-atom parameters constrained	

Table 3

Cremer & Pople (1975) conformational parameters for the rings in (II).

Ring	q_2 (Å)	Conformation
<i>A</i>	0.318 (2)	Twist-envelope
<i>B</i>	0.399 (2)	Twist-envelope

H atoms were fixed geometrically at calculated positions and allowed to ride on their attached atoms (C–H = 0.97 or 0.98 Å).

For both compounds, data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1995); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Johnson & Burnett, 1996; Farrugia, 1999); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1610). Services for accessing these data are described at the back of the journal.

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