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4,8-Bis(3,4-methylenedioxy)phenyl-3,7-dioxabicyclo[3.3.0]octan-2-one

Simon J. Coles* and Michael B. Hursthouse

Department of Chemistry, University of Southampton, Southampton SO17 1BJ, England

Correspondence e-mail: s.j.coles@soton.ac.uk

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The title compound, $C_{20}H_{16}O_7$, is an intermediate in the total synthesis of (±)-asarinin. The molecular structure contains four chiral centres and crystallizes as two independent molecules. The chirality of the two molecules is the same, but they adopt different conformations. The compound is enantiomeric, with the second enantiomer arising from the centrosymmetric nature of the space group.

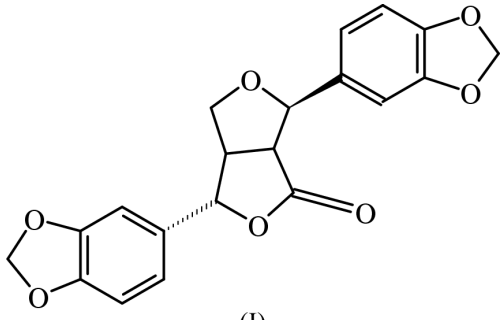
Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.006 Å
R factor = 0.063
wR factor = 0.148
Data-to-parameter ratio = 14.5

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

Comment

The title compound, (I), was prepared in the course of studies towards the synthesis of furofuran lignans. The compound is an intermediate in the total synthesis of (±)-asarinin (Brown & Hinks, 1998).



(I)

Compound (I) crystallizes with two molecules in the asymmetric unit, with bonds lengths agreeing with each other and with standard distances (Allen *et al.*, 1987). The two molecules do, however, exhibit some conformational differences in the central fused ring part of the molecule. There are four chiral sites in the central fused-ring moiety of the molecule, which induces a twist in the molecular conformation (molecule *A*: C1 = *R*, C2 = *S*, C3 = *R*, C5 = *S*; molecule *B*: C21 = *R*, C22 = *S*, C23 = *R*, C25 = *S*). As the space group is centrosymmetric, a second enantiomer is produced by a symmetry operation on the molecule through the inversion centre. Despite these sites having the same chirality in molecules *A* and *B*, the ring conformations differ. The ring conformations may be described by puckering analysis (Cremer & Pople, 1975) and local pseudosymmetry (Duax *et al.*, 1976) thus: ring C1–C4/O1: Q_T = 0.411 (3) Å, pseudo-mirror along O1 and pseudo-twofold axis along C2, conformation intermediate between envelope and half-chair; ring C2/C3/C5/C6/O2: Q_T = 0.070 (4) Å, practically planar with a pseudo-twofold axis along O2 and a pseudo-mirror along C2, conformation intermediate between half-chair and envelope; ring C21–C24/O8: Q_Ti = 0.421 (3) Å, pseudo-twofold axis

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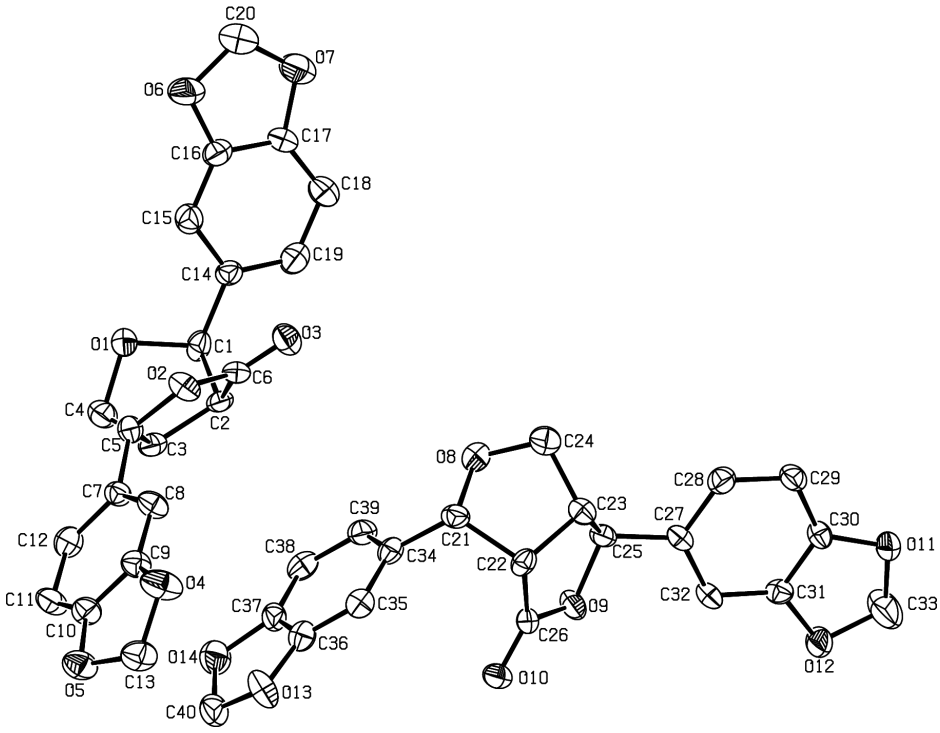

Figure 1
View of the two independent molecules of the title compound (50% probability displacement ellipsoids).

along C22, conformation half-chair; ring C22/C23/C25/C26/O9: Q_T = 0.153 (4) Å, pseudo-mirror along C23, conformation envelope. In addition, the dioxa-rings show some significant puckering, with Q_T ranging from 0.091 (4) to 0.202 (4) Å in envelope conformations, with the methylene C atoms at the flaps. An overlay plot of the two molecules shows that there is a 180° rotation about the C1—C14 bond so that the (3,4-methylenedioxy)phenyl groups, on one end of the molecule only, are non-superimposable mirror images of each other.

A number of weak intermolecular interactions (which are not classical hydrogen bonds) are present, forming an infinite two-dimensional sheet. The donor–acceptor distances all have H···O contacts less than the sum of Pauling's van der Waals radii (2.60 Å) and are C33···O3^{i} = 3.002 (6) Å, C40···O4^{ii} = 3.144 (5) Å, C4···O1^{iii} = 3.426 (5) Å and C5···O1^{iii} = 3.509 (5) Å [symmetry codes: (i) $\frac{3}{2}-x, \frac{3}{2}-y, \frac{1}{2}-z$; (ii) $x, 2\ y, z$; (iii) $2-x, -y, -z$].

Experimental

The title compound was prepared following a method previously reported (Brown & Hinks, 1998) and the furofuranone product was recrystallized from an EtOAc/hexane mixture.

Crystal data

$C_{20}H_{16}O_7$
M_r = 368.33
Monoclinic, $P2_1/n$
a = 12.996 (3) Å
b = 5.8243 (12) Å
c = 42.693 (9) Å
β = 97.42 (3)°
V = 3204.4 (11) Å^3
Z = 8
D_x = 1.527 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25343 reflections
θ = 2.9–27.5°
μ = 0.12 mm^{-1}
T = 150 (2) K
Needle/plate, colourless
0.20 × 0.05 × 0.01 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans to fill Ewald sphere
Absorption correction: multi-scan (Blessing, 1997)
T_{min} = 0.977, T_{max} = 0.999
34 875 measured reflections
7091 independent reflections
2259 reflections with $I > 2\sigma(I)$
R_{int} = 0.229
θ_{max} = 27.5°
$h = -16 \rightarrow 16$
$k = -7 \rightarrow 7$
$l = -54 \rightarrow 55$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.063
$wR(F^2)$ = 0.148
S = 0.87
7091 reflections
488 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0439P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.017
$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.30 e Å^{-3}

A high value of R_{int} was observed and is due to merging a high number of weak reflections [$I > 2\sigma(I)$/independent reflections = 0.319] with relatively high standard uncertainties. All H atoms were placed in idealized positions with displacement parameters tied to those of the parent atoms. The extinction parameter refined to zero. An elongation of the ellipsoid of C33 perpendicular to the plane of the ring indicates slight disorder of this envelope atom.

Cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Hooft, 1998); data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1990).

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