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(4a*S**,7a*R**)-2,10-Dioxoperhydrobenzo[*d*]-naphthalene

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The title racemic compound, $C_{14}H_{20}O_2$, a tricylic diketone isolated from enamine reactions of cyclohexanone with methyl vinyl ketone, is shown to have an all-chair conformation and a *cis* stereochemical relationship for its methine H atoms.

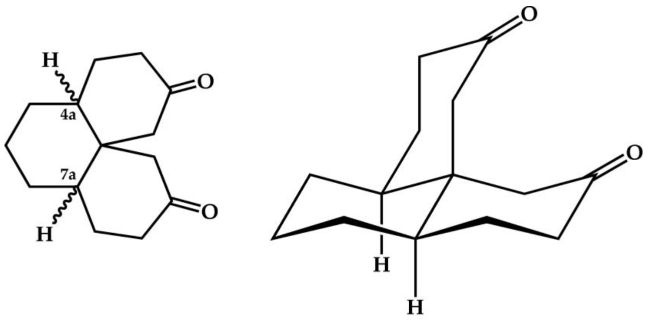
Key indicators

Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.005 Å
R factor = 0.045
wR factor = 0.086
Data-to-parameter ratio = 7.9

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

Comment

Among the isolable by-products from the Robinson annulation of cyclohexanone *via* the enamine (Stork *et al.*, 1963) is a diastereomeric pair or set of tricyclic diketones arising from reaction with two equivalents of methyl vinyl ketone. With intentional excesses of reagent, these compounds appear in higher yield (House *et al.*, 1965). Although three diastereomers could, in theory, result, the skeletal connectivity admits of only two that allow all rings to assume chair conformations. Of these two, one has *cis* and the other *trans* stereochemistry for the two methine H atoms. Since both materials have been identified (however, see below), the known isomers are most simply differentiated by reference to this *cis*/*trans* stereochemistry.



(I)

Historically, the earliest, and highest-melting (433 K), isomer to be isolated (House *et al.*, 1965) was assigned the stereochemistry shown in (I), which is confirmed in the present report (Fig. 1). That assignment was bolstered in 1975 (Wilcox & Grantham, 1975) by a ^{13}C NMR spectrum showing 14 peaks, consistent with the absence of symmetry in (I), whereas either *trans* isomer should have a C_2 axis. Subsequently, Bergman & Migron (1976) isolated a second isomer (m.p. 399 K), which they differentiated from (I) by dipole-moment measurements and assigned the all-chair *trans* structure. Hickmott & Simpson (1992) have since reported the isolation of a low-melting (408 K) isomer that has seven ^{13}C peaks, but it remains unclear whether this differs from Bergman & Migron's 399 K material. Hickmott *et al.* (1990, 1992) have also reported crystal structures for 4*a*-methylated analogs of both (I) and the all-chair *trans* species.

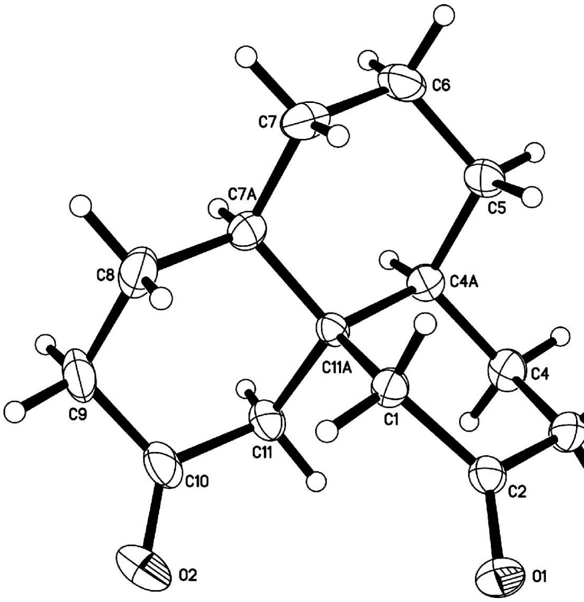


Figure 1
The molecular structure of (I) with the numbering scheme. Displacement ellipsoids are drawn at the 20% probability level.

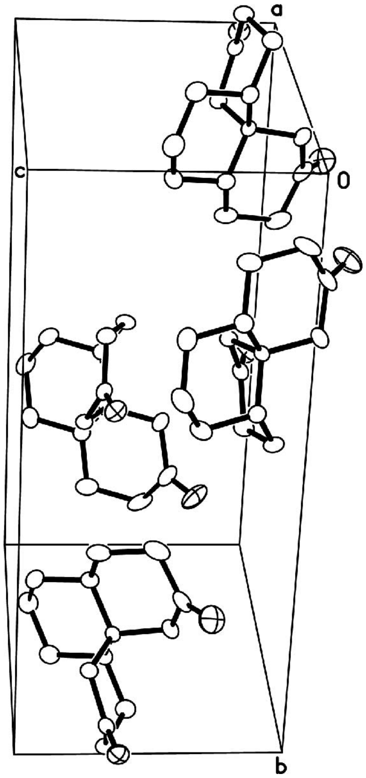


Figure 2
A packing diagram for (I), with all H atoms removed for clarity. Displacement ellipsoids are drawn at the 20% probability level.

Although (I) is racemic and both enantiomers are present in the unit cell, the space group ($Pna2_1$) is non-centrosymmetric (Fig. 2). Within the 2.7 Å range we survey for non-bonded C—H···O interactions (Steiner, 1997), one close contact was found (Table 1), to O1 from H3*B* in a screw-related molecule.

Experimental

Compound (I) was isolated as a by-product from a sequential reaction of the pyrrolidine enamine of cyclohexanone with ethyl bromoacetate and methyl vinyl ketone (Davison *et al.*, 2004). Crystals of (I) suitable for X-ray study were produced by refrigeration of an acetone–hexane solution (m.p. 435 K).

Crystal data

$C_{14}H_{20}O_2$
$M_r = 220.30$
Orthorhombic, $Pna2_1$
$a = 10.618\ (3)$ Å
$b = 16.224\ (4)$ Å
$c = 6.9661\ (15)$ Å
$V = 1200.0\ (5)$ Å^3
$Z = 4$
$D_x = 1.219$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 33 reflections
$\theta = 2.3$–$9.9°$
$\mu = 0.08$ mm^{-1}
$T = 296\ (2)$ K
Parallelepiped, colorless
0.50 × 0.19 × 0.19 mm

Data collection

Siemens *P*4 diffractometer
$\omega/2\theta$ scans
Absorption correction: numerical (*SHELXTL*; Sheldrick, 1997)
$T_{\min} = 0.975$, $T_{\max} = 0.983$
2308 measured reflections
1154 independent reflections
725 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.056$
$\theta_{\max} = 25.0°$
$h = -12 \rightarrow 12$
$k = -19 \rightarrow 19$
$l = -8 \rightarrow 8$
3 standard reflections every 97 reflections intensity decay: <1.2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.086$
$S = 1.01$
1154 reflections
146 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0192P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.13$ e Å^{-3}
$\Delta\rho_{\min} = -0.12$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.022 (3)

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C3—H3*B*···O1$^{\rm i}$	0.97	2.575	3.374 (6)	140

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

All H atoms were found in difference density maps but were placed in calculated positions and allowed to refine as riding on their respective C atoms, with C—H = 0.97–0.98 Å and $U_{\rm iso}$(H) = $1.2U_{\rm eq}$(C). Because of negligible anomalous scattering effects, Friedel pairs were averaged in the refinement.

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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