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(±)-(*cis*-8a-Hydroxy-2-oxoperhydronaphthalen-4a-yl)propanenitrile: hydrogen bonding in a Robinson-annulation intermediate

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The title racemate, $C_{13}H_{19}NO_2$, is a pre-dehydration intermediate isolated from the base-catalysed Robinson annulation of (+/−)-2-(2-cyanoethyl)cyclohexanone. Centrosymmetric dimers are formed by reciprocal hydroxyl-to-ketone hydrogen bonding [O···O = 2.7902 (13) Å and O—H···O = 176°]. One intermolecular C—H···O close contact is found to the hydroxyl group.

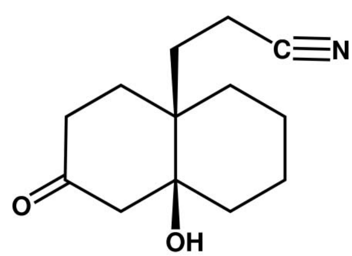
Key indicators

Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.002 Å
R factor = 0.037
wR factor = 0.096
Data-to-parameter ratio = 12.7

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

Comment

An interest in decalin-based keto acids led us to Robinson annulations of several 2-substituted cyclohexanones utilizing a variety of catalysts (Zewge *et al.*, 1998, 1999, 2006; Davison *et al.*, 2004). One such base-catalysed reaction provided a crystalline material, (I), shown by X-ray crystallography to have a β-hydroxyketone structure.



(I)

Fig. 1 illustrates the molecular structure of (I) and the conformation it adopts. The steroid-like conformation of *cis*-decalone (Djerassi, 1960) places the cyanoethyl substituent equatorial relative to the ketone ring. The energy advantage

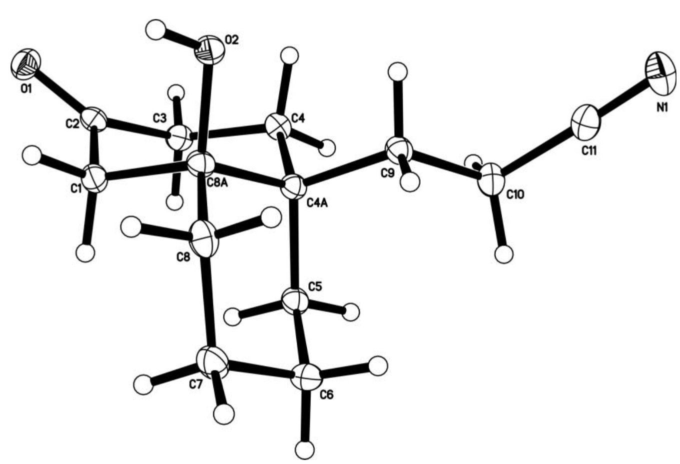


Figure 1
The molecular structure of (I) with the atom numbering. Displacement ellipsoids are drawn at the 40% probability level.

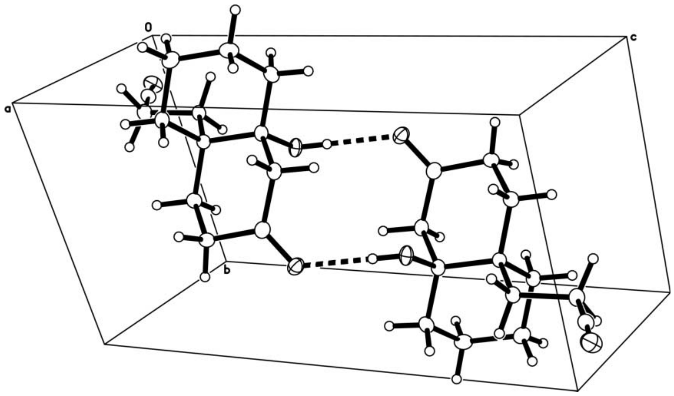


Figure 2
A partial packing diagram for (I), with all C-bound H atoms removed for clarity, illustrating the centrosymmetric dimerization of asymmetric units around $\frac{1}{2},\frac{1}{2},\frac{1}{2}$ in the chosen cell. Displacement ellipsoids are drawn at the 40% probability level. Hydrogen bonds are shown as dashed lines.

of this within the asymmetric unit is unclear, but may involve the reciprocal hydrogen bonding in the packing, which is permitted by the observed *cisoid* orientation of ketone and hydroxyl groups but is impossible in the alternative all-chair conformer.

Fig. 2 shows the hydrogen-bonding aggregation of (I), which consists of centrosymmetric hydroxyl-to-ketone dimerization (Table 1). Since $Z = 2$, these dimers repeat translationally in the packing. We characterize the geometry of hydrogen bonding to carbonyls using a combination of the H···O═C angle and the H···O═C—C torsion angle. These describe the approach of the H atom to the receptor O atom in terms of its deviation from, respectively, C═O axiality (ideal = 120°) and planarity with the carbonyl (ideal = 0°). In (I), these angles are 127 and 3°. Although both O atoms are buried toward the center of the dimeric unit, one intermolecular C—H···O close contact was found (Table 1) within the range we standardly survey for such interactions; no C—H···N contacts were found.

Compound (I) arises *via* normal Michael addition to methyl vinyl ketone (MVK) from the more-substituted cyclohexanone α-position (House, 1972), followed by internal aldol condensation, stopping short of dehydration. Although (I) is previously unreported, there is ample precedent for isolation of such pre-dehydration intermediates in Robinson annulations (Bergmann *et al.*, 1959). Indeed, specific techniques exist designed to isolate such β-hydroxyketones, which may then be dehydrated in a separate step, as we did with (I).

Given racemic and achiral starting materials, the only stereoisomerism possible in the bicyclic product involves a *cis versus* a *trans* ring juncture. There is no inherent impediment to the formation of *trans* isomers in such cases, and several instances exist of the isolation of *trans* compounds and of epimeric mixtures. However, in simple 2-decalone systems with substituents at both ring-juncture positions, *cis* isomers, like (I), will normally have fewer unfavorable steric interactions and should be more stable than the corresponding *trans* species.

Experimental

Compound (I) was isolated from a reaction in which methanolic MVK (196 mmol) was added slowly to an ice-cold methanolic solution of cyanoketone (+/−)-2-(2-cyanoethyl)cyclohexanone (196 mmol) and sodium methoxide (12 mmol). After overnight storage in a freezer, the mixture was worked up as usual, briefly treated at room temperature with ethanolic KOH and neutralized. Fractional distillation and refrigeration then yielded crystalline material: 8.2% of (I) from the higher-boiling fraction, accompanied by 8.7% of its dehydration product (m.p. 359 K) from the lower-boiling one. Crystals of (I) suitable for X-ray crystallographic analysis were obtained from diethyl ether (m.p. 424 K).

Crystal data

$C_{13}H_{19}NO_2$	$V = 579.89$ (13) Å^3
$M_r = 221.29$	$Z = 2$
Triclinic, $P\overline{1}$	$D_x = 1.267$ Mg m^{-3}
$a = 5.8894$ (7) Å	Cu $K\alpha$ radiation
$b = 7.6197$ (11) Å	$\mu = 0.68$ mm^{-1}
$c = 13.4112$ (17) Å	$T = 100$ (2) K
$\alpha = 91.860$ (7)°	Parallelepiped, colorless
$\beta = 91.695$ (5)°	0.33 × 0.24 × 0.15 mm
$\gamma = 105.246$ (6)°	

Data collection

Bruker SMART CCD APEX-II area-detector diffractometer	4494 measured reflections
φ and ω scans	1857 independent reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)	1806 reflections with $I > 2\sigma(I)$
$T_{min} = 0.82$, $T_{max} = 0.90$	$R_{int} = 0.016$
	$\theta_{max} = 67.5°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0464P)^2 + 0.2474P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.037$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.096$	$\Delta\rho_{max} = 0.32$ e Å^{-3}
$S = 1.08$	$\Delta\rho_{min} = -0.20$ e Å^{-3}
1857 reflections	
146 parameters	
H-atom parameters constrained	

Table 1
Hydrogen-bond and close-contact geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2A···O1^{i}	0.84	1.95	2.7902 (13)	176
C3—H3B···O2^{ii}	0.99	2.47	3.3184 (15)	144

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

All H atoms were found in electron difference density maps. The O-bound H atom was constrained to an idealized position with its distance fixed at 0.84 Å and $U_{iso}(H) = 1.5U_{eq}(O)$. Methylene H atoms were placed in geometrically idealized positions and constrained to ride on their parent C atoms with C—H = 0.99 Å and $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *APEX2* (Bruker, 2006); cell refinement: *APEX2*; data reduction: *SAINT* (Bruker, 2005); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 2004); software used to prepare material for publication: *SHELXTL*.

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