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The Relative Configuration of 8-[(2,2-Dimethyl-3-oxocyclohexyl)hydroxymethyl]-1-methylbicyclo[4.2.0]octan-7-one, $C_{18}H_{28}O_3$

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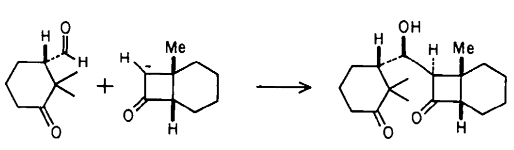
Abstract. $M_r = 292{\cdot}42$, monoclinic, $P2_1/c$, $a = 7{\cdot}095\,(3)$, $b = 11{\cdot}584\,(6)$, $c = 20{\cdot}191\,(7)$ Å, $\beta = 95{\cdot}05\,(3)^\circ$, $V = 1653\,(2)$ Å^3, $Z = 4$, $D_x = 1{\cdot}175\,(1)$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å, $\mu = 0{\cdot}73$ cm^{-1}, $F(000) = 640$, $T = 140\,(5)$ K, final discrepancy factor $R_F = 4{\cdot}1\%$ for 1665 unique reflections above $2\sigma(I)$ in the range $4 < 2\theta < 45^\circ$. The title compound, an aldol, was obtained as an intermediate in a synthesis of the taxane skeleton. Both cyclohexane rings are in the chair conformation. The cyclobutanone is in an envelope conformation with a dihedral angle of 26·1 (2)°. Bond angles and distances are normal. Although the compound is an aldol, there is no intramolecular hydrogen bond between the cyclobutanone carbonyl and the hydroxy group in the crystal.

Introduction. The compound was the product of the aldol reaction of the cyclobutanone enolate (2) with 2,2-dimethyl-3-oxocyclohexanecarbaldehyde (3) (Clark, Lin & Nikaido, 1984). This reaction generates two chiral centers, C(7) and C(9), and in addition selects one enantiomer of the racemic mixture of the aldehyde to react with a single enantiomer of the enolate. Thus, four chiral centers – C(7), C(8), C(9) and C(10) – are juxtaposed in a single operation. It was anticipated that a mixture of products would result. A comparison of the spectral characteristics of the individual components should allow secure structural assignment. However, the aldol reaction gave a single product, (1).



(3) (2) (1)

Assignment of relative configuration using the latest two-dimensional NMR techniques was thwarted because the dihedral angle between the hydrogens attached to C(9) and C(10) is 90° in solution, and therefore $J(H_9H_{10}) = 0$. Since single crystals could readily be obtained, structure determination using X-ray diffraction was undertaken.

Experimental. Crystals obtained by recrystallization from hexane–dichloromethane; prismatic, 0·4 × 0·3 × 0·2 mm; Enraf–Nonius CAD-4 diffractometer; systematic absences $h0l$, l odd and $0k0$, k odd; unit-cell parameters from 25 centered reflections ($2\theta = 15$–30°); no absorption correction; hkl range: $h = -7$ to 7, $k = 0$–12, $l = 0$–21 (also negative l from 0–24 in 2θ). 2526 reflections with $2\theta < 45^\circ$. 3 standards measured every 1 h of X-ray exposure, no significant changes. 2035 unique reflections [$R_{\rm int}$(merging) = 1·9%]. 370 unobserved reflections [$I < 2\sigma(I)$]. Structure solved by direct methods; hydrogens located by difference Fourier techniques and calculation. Positional parameters refined for all H atoms. Isotropic temperature factor for the hydroxy H atom fixed at 3·0 Å^2; for all other H atoms fixed at 2·0 Å^2. 274 variables refined. $\sum w(|F_o| - |F_c|)^2$ minimized, $w^{-1} = [\sigma^2_{\rm counting}(F_o^2) + (0{\cdot}05F_o^2)^2]/4F_o^2$. $R = 4{\cdot}1$, $wR = 6{\cdot}9\%$, $S = 1{\cdot}705$. Max. Δ/σ in last cycle = 0·01. $\Delta\rho_{\rm max}$ on final difference Fourier map = 0·2 e Å^{-3}. Scattering factors including f' and f'' values from *International Tables for X-ray Crystallography* (1974). Computation on PDP 11/34 computer using Enraf–Nonius (1983) *SDP-Plus* programs. The positional parameters for the non-hydrogen atoms are listed in Table 1.*

Discussion. The structure of (1) is shown in Fig. 1 and the bond distances and angles are given in Table 2. The puckering of the cyclobutane ring is indicated by the dihedral angle of 26·1° between the planes defined by the atoms C(5)—C(6)—C(7) and C(5)—C(8)—C(7). The crystal structure shows that the aldehyde approaches the enolate from the least-hindered *exo* face, thereby setting the configuration at C(7) as *β*. The adjacent center, C(8), bears a hydroxy substituent and the relative configuration of the hydroxy group to the C(7) center is *threo*, following the usage introduced by Dubois & Dubois (1967). This stereochemistry can be rationalized as arising from the six-membered ring

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* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and bond lengths and angles involving H have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39773 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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chelate transition state first proposed by these authors and subsequently used by several workers (Heathcock, 1982, and references therein; Evans, Nelson & Taber, 1982, and references therein). Finally, the next center is the result of Cram-type (Cram & Elhafez, 1952) attack on the aldehyde by the enolate. Thus, this product is demonstrated to be the *threo*, Cram adduct.

The relative configurations of aldols have conventionally been assigned from the ^{1}H NMR spectra; most notably, from the coupling constant observed between the two methine hydrogen atoms [in this case, the hydrogen atoms on C(7) and C(9)] (Heathcock & White, 1979; Heathcock, White, Morrison & VanDerveer, 1981; Heathcock, Pirrung, Buse, Hagen, Young & Sohn, 1979; Heathcock, Buse, Keschick, Pirrung, Sohn & Lampe, 1980; Heathcock, Pirrung, Lampe, Buse & Young, 1981; House, Crumrine, Teranishi & Olmstead, 1973). The rationale for doing this is that the aldol itself should exist in solution as a six-membered ring in which the hydroxyl hydrogen atom hydrogen bonds to the ketone. This imposes a specific conformation on the aldol, which allows the coupling constant to be diagnostic (House *et al.*, 1973, and references therein; Evans *et al.*, 1982, and references therein). As shown in Fig. 1, the hydroxyl does not hydrogen bond intramolecularly to the cyclobutanone carbonyl. Rather, there is an intermolecular hydrogen bond. Thus, the crystal structure does not show the structural feature assumed to be diagnostic for the assignment of the relative stereochemistry of aldols.

Table 1. *Positional parameters and their e.s.d.'s*

	x	y	z	B_{eq}(Å^2)*
O(1)	0·0610 (2)	0·2903 (2)	0·8182 (1)	2·61 (4)
O(2)	0·3329 (2)	0·0990 (1)	0·91599 (8)	1·71 (3)
O(3)	0·5600 (2)	0·1288 (1)	1·06173 (9)	2·13 (4)
C(1)	0·2585 (3)	0·1020 (2)	0·6851 (1)	1·69 (5)
C(2)	0·0842 (3)	0·0576 (2)	0·6431 (1)	2·16 (6)
C(3)	−0·0929 (3)	0·1088 (2)	0·6681 (1)	2·42 (6)
C(4)	−0·1152 (3)	0·0705 (2)	0·7386 (1)	2·20 (5)
C(5)	0·0673 (3)	0·0840 (2)	0·7842 (1)	1·65 (5)
C(6)	0·1388 (3)	0·2008 (2)	0·8070 (1)	1·72 (5)
C(7)	0·3467 (3)	0·1663 (2)	0·8032 (1)	1·50 (5)
C(8)	0·2648 (3)	0·0647 (2)	0·7576 (1)	1·51 (5)
C(8′)	0·3490 (3)	−0·0552 (2)	0·7682 (1)	1·78 (5)
C(9)	0·4588 (3)	0·1367 (2)	0·8692 (1)	1·54 (5)
C(10)	0·5813 (3)	0·2377 (2)	0·8977 (1)	1·54 (5)
C(11)	0·6894 (3)	0·2052 (2)	0·9654 (1)	1·70 (5)
C(12)	0·5547 (3)	0·2040 (2)	1·0193 (1)	1·71 (5)
C(13)	0·4248 (3)	0·3065 (2)	1·0235 (1)	1·98 (5)
C(14)	0·3322 (3)	0·3459 (2)	0·9561 (1)	1·92 (5)
C(15)	0·4708 (3)	0·3510 (2)	0·9032 (1)	1·79 (5)
C(16)	0·8387 (3)	0·2995 (2)	0·9852 (1)	2·29 (6)
C(17)	0·7953 (3)	0·0903 (2)	0·9619 (1)	2·14 (6)

* $B_{eq} = \frac{4}{3}[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\alpha)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

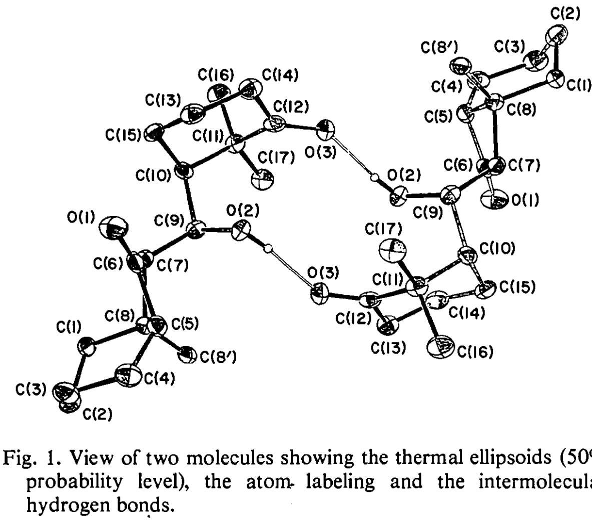

Fig. 1. View of two molecules showing the thermal ellipsoids (50% probability level), the atom labeling and the intermolecular hydrogen bonds.

Table 2. *Bond distances* (Å) *and angles* (°) *involving non-hydrogen atoms*

O(1)—C(6)	1·205 (2)	C(8)—C(8′)	1·519 (3)
O(2)—C(9)	1·424 (2)	C(9)—C(10)	1·539 (3)
O(3)—C(12)	1·221 (3)	C(10)—C(11)	1·554 (3)
C(1)—C(2)	1·527 (3)	O(2)—O(3)	2·770 (2)
C(1)—C(8)	1·522 (3)	C(10)—C(15)	1·537 (3)
C(2)—C(3)	1·515 (3)	C(11)—C(12)	1·509 (3)
C(3)—C(4)	1·512 (3)	C(11)—C(16)	1·549 (3)
C(4)—C(5)	1·530 (3)	C(11)—C(17)	1·533 (3)
C(5)—C(6)	1·503 (3)	C(12)—C(13)	1·509 (3)
C(5)—C(8)	1·559 (3)	C(13)—C(14)	1·528 (3)
C(6)—C(7)	1·536 (3)	C(14)—C(15)	1·515 (3)
C(7)—C(8)	1·547 (3)	H(O2)—O(2)	0·83 (3)
C(7)—C(9)	1·529 (3)	H(O2)—O(3)	1·94 (3)

C(2)—C(1)—C(8)	113·1 (2)	C(5)—C(8)—C(7)	89·3 (2)
C(6)—C(5)—C(8)	86·9 (1)	C(5)—C(8)—C(8′)	115·9 (2)
C(8)—C(7)—C(9)	118·6 (2)	C(7)—C(8)—C(8′)	118·7 (2)
C(11)—C(10)—C(15)	111·0 (2)	O(2)—C(9)—C(7)	109·8 (2)
C(12)—C(11)—C(16)	106·4 (2)	O(2)—C(9)—C(10)	110·5 (2)
C(12)—C(11)—C(17)	111·6 (2)	C(7)—C(9)—C(10)	112·9 (2)
C(16)—C(11)—C(17)	107·3 (2)	C(9)—C(10)—C(11)	111·3 (2)
C(2)—C(1)—C(8)	113·1 (2)	C(9)—C(10)—C(15)	113·7 (2)
C(1)—C(2)—C(3)	109·7 (2)	C(11)—C(10)—C(15)	111·0 (2)
C(2)—C(3)—C(4)	111·0 (2)	C(10)—C(11)—C(12)	109·9 (2)
C(3)—C(4)—C(5)	112·5 (2)	C(10)—C(11)—C(16)	109·3 (2)
C(4)—C(5)—C(6)	121·4 (2)	C(10)—C(11)—C(17)	112·1 (2)
C(4)—C(5)—C(8)	121·1 (2)	C(12)—C(11)—C(16)	106·4 (2)
C(6)—C(5)—C(8)	86·9 (1)	C(12)—C(11)—C(17)	111·6 (2)
O(1)—C(6)—C(5)	133·2 (2)	C(16)—C(11)—C(17)	107·3 (2)
O(1)—C(6)—C(7)	133·7 (2)	O(3)—C(12)—C(11)	122·0 (2)
C(5)—C(6)—C(7)	92·9 (2)	O(3)—C(12)—C(13)	120·2 (2)
C(6)—C(7)—C(8)	85·2 (1)	C(11)—C(12)—C(13)	117·5 (2)
C(6)—C(7)—C(9)	116·3 (2)	C(12)—C(13)—C(14)	113·6 (2)
C(8)—C(7)—C(9)	118·6 (2)	C(13)—C(14)—C(15)	112·6 (2)
C(1)—C(8)—C(5)	109·8 (2)	C(10)—C(15)—C(14)	112·6 (2)
C(1)—C(8)—C(7)	109·2 (2)	O(2)—H(O2)—O(3)	171·2 (2)
C(1)—C(8)—C(8′)	111·9 (2)		

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Acta Cryst. (1985). C**41**, 157–158

Structures of a hydrocarbon $C_{58}H_{40}$ and its photo-oxidation products. I. 1,1,2,3,4,5,6-Heptaphenyl-1,4-dihydrobenz[*e*]-*as*-indacene – a new determination.

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Abstract

$M_r = 736\cdot95$, triclinic, $P\bar{1}$, $a = 11\cdot903\ (4)$, $b = 18\cdot433\ (6)$, $c = 10\cdot035\ (4)$ Å, $\alpha = 107\cdot05\ (3)$, $\beta = 95\cdot42\ (3)$, $\gamma = 98\cdot76\ (3)^\circ$, $V = 2058\ (2)$ Å^3, $Z = 2$, $D_x = 1\cdot190$ Mg m^{-3}, Cu $K\alpha_1$, $\lambda = 1\cdot5404$ Å, $\mu = 0\cdot528$ mm^{-1}, $F(000) = 776$, $T = 295\ (2)$ K, $R = 0\cdot043$ for 5993 observed data $[I > 3\sigma(I)]$, 0·068 for all 7823 data. The sample was provided by M. J. Gallagher and I. D. Jenkins of the School of Chemistry, the University of New South Wales. With a different set of reflection data and a different unit cell, the molecular structure essentially agrees with that determined independently by Shoja, Espiritu, White & Borowitz [*Acta Cryst.* (1980), B**36**, 1967–1969].

Introduction

The molecular structure of this hydrocarbon $C_{58}H_{40}$ (I) (Fig. 1) and those of two isomeric photo-oxidation products (II) and (III) of formula $C_{58}H_{40}O_2$, referred to as (*B*) and (*A*) respectively by Gallagher & Jenkins (1969, p.2613), who prepared all three, could not be determined by chemical means. The structure of (II) has been solved by diffraction methods (Grainger, 1984). Work on (III) continues.

Shoja, Espiritu, White & Borowitz (1980) (hereafter Shoja) and this study have independently found essentially the same structure for (I), and complement one another in regard to the accuracies of determining the unit cell and atomic coordinates.

Experimental

Tabular crystal 0·5 × 0·3 × 0·15 mm; Ni-filtered Cu radiation; Siemens AED diffractometer; $(\sin\theta)/\lambda$ to 0·61 Å^{-1}; absorption correction on 64-point grid; 7823 unique reflections measured, 1830 unobserved $[I < 3\sigma(I)]$; $h = -14$ to 14, $k = -22$ to 21, $l = 0$ to 12. Intensity statistics indicated $P\bar{1}$. Structure solved by direct methods (*MULTAN*80), refined on $|F|$ by blocked-matrix least squares (one block each for the 7 phenyl rings and another for the remaining parameters) on 'observed' data; H atoms in calculated positions at 1·0 Å with temperature parameters set equal to those of bonded atoms; refined scale factor, isotropic extinction correction parameter, positional and anisotropic thermal parameters for non-hydrogen atoms (524

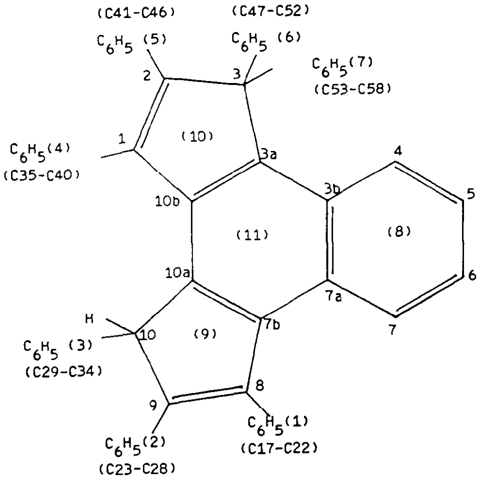

Fig. 1. Structural formula and atomic labels for the hydrocarbon $C_{58}H_{40}$. (Note that the crystallographic numbering differs from that used in the title.)

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