Discussion. The final atomic coordinates are reported in Table 1. Our results agree fairly well with the previous work.* The main bond distances and angles are listed in Table 2. The clearly defined thiocation is pyramidal, suggesting sp^3 hybridization of the sulfur. Although containing only one symmetry plane (for y = 0·25 or 0·75), in which are located I, S and C(1) atoms, the thiocation approximates very well to the 3m symmetry assigned to the free ion: the C—S—C bond angles are equal, 101·4° (4), and the bond distances differ by very little, 1·785 and 1·805 Å. The structure (shown in Figs. 1 and 2) may be approximately described as a distorted NaCl structure, each ion being surrounded by six of the opposite charge (Zuccaro & McCullough, 1959).

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53395 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1991). C47, 984–985

Structure of (±)-(2*S*,1′*S*)-2-[Hydroxy(phenyl)methyl]-2-methylcyclohexanone, $C_{14}H_{18}O_2$

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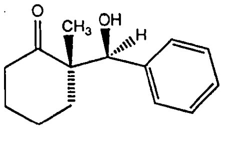
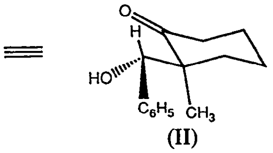
(*Received* 25 *November* 1985; *accepted* 8 *August* 1990)

Abstract. M_r = 281·30, monoclinic, $P2_1/n$, a = 10·966 (4), b = 7·170 (3), c = 15·976 (4) Å, β = 93·14 (2)°, V = 1254·3 (9) Å^3, Z = 4, D_x = 1·16 g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ = 0·706 cm^{-1}, F(000) = 472, T = 295 K, final R = 0·057 for 1212 unique observed reflections. The compound was prepared by reaction of the trichlorotitanium-$\Delta^{1(2)}$-enolate of 2-methylcyclohexanone with benzaldehyde.

Introduction. The stereochemistry of the major aldol isomer formed in the reaction of the trichlorotitanium-$\Delta^{1(2)}$-enolate of 2-methylcyclohexanone and benzaldehyde is depicted below. This compound has played a pivotal role in the recent re-evaluation of the boat transition state of aldol reactions in general (Nakamura & Kuwajima, 1983; Hoffmann, Ditrich & Froch, 1985). The nature of (I) does not permit the application of ^{1}H NMR spectroscopy (Heathcock, 1983) for the determination of its relative stereochemistry since it is fully substituted at the α-carbon. Hence, the proton on C(8) does not provide any stereochemical information although it is noted that in the NMR spectrum, taken in CCl_4, the C(8) proton signal appears at a higher field than that of the diastereomeric adduct.



(I)



(II)

A crystal structure analysis of (I), prepared according to the procedure of Nakamura & Kuwajima (1983), was undertaken to determine unambiguously all aspects of the stereochemistry of this compound.

Experimental. Clear, colorless crystal of the aldol, (I), 0·25 × 0·27 × 0·30 mm, m.p. 337·5–339 K, aligned on Nicolet $R3m/E$ diffractometer with an Mo target, normal focus tube, graphite monochromator

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and 0·5 mm pinhole collimator. Lattice parameters calculated from 25 reflections with $25 \leq 2\theta \leq 27°$. Total of 1888 reflections measured (at 295 K) over a period of 30 h utilizing the $\theta/2\theta$ scan technique within the ranges $3{\cdot}5 \leq 2\theta \leq 45°$, h −12–12, k 0–8, l 0–18. Systematic absences found on $h0l$ layer for $h + l = 2n + 1$ and $0k0$ for $k = 2n + 1$. Intensities of three standard reflections (008, 020, 600) recorded after every 97 reflections. Total of 60 standard reflections, decreasing linearly by 2·7%, used to correct the intensities of the remaining 1212 unique observed reflections $[F_o > 2{\cdot}5\sigma(F_o)]$, $R_{\rm int} = 0{\cdot}017$. Data corrected for Lorentz and polarization effects. No absorption correction applied. All 16 non-H atoms immediately located by direct-methods structure solution (*SHELXTL*; Sheldrick, 1984). Remaining 18 H atoms located in subsequent difference Fourier syntheses. Structure refined by block-diagonal least squares with anisotropic thermal parameters for all but H atoms, minimizing $\sum w(|F_o| - |F_c|)^2$. H-atom isotropic thermal parameters taken as 1·2 times the equivalent isotropic parameter of the bonded atom. H-atom positional parameters fixed in calculated positions in the final stages of refinement. The final $R = 0{\cdot}057$ and $wR = 0{\cdot}049$ for 145 variables with $w = 1/[\sigma(F_o)^2 + 0{\cdot}0001(F_o)^2]$ and $S = 1{\cdot}16$. In the last cycle of refinement $(\Delta/\sigma)_{\max}$ was 0·039 and in the final difference Fourier synthesis $(\Delta\rho)_{\max} < 0{\cdot}2$ e Å^{-3}. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). All computer programs belong to the *SHELXTL* system (Sheldrick, 1984).

Table 1. *Atom coordinates* (× 10^4) *and temperature factors* (Å^2 × 10^3)

	x	y	z	U*
O(1)	3817 (2)	−1836 (3)	8656 (1)	85 (1)
O(2)	1708 (2)	299 (3)	7490 (1)	60 (1)
C(1)	3503 (3)	−208 (4)	8701 (2)	62 (1)
C(2)	2231 (3)	348 (4)	8954 (2)	53 (1)
C(3)	2429 (3)	1579 (4)	9744 (2)	65 (1)
C(4)	3288 (3)	3215 (4)	9645 (2)	76 (1)
C(5)	4520 (3)	2577 (5)	9353 (2)	85 (2)
C(6)	4388 (3)	1352 (4)	8574 (2)	75 (1)
C(7)	1492 (3)	−1374 (4)	9156 (2)	82 (1)
C(8)	1617 (2)	1456 (4)	8212 (2)	50 (1)
C(9)	318 (3)	2037 (4)	8328 (2)	53 (1)
C(10)	71 (3)	3767 (4)	8655 (2)	68 (1)
C(11)	−1113 (4)	4362 (5)	8754 (2)	88 (2)
C(12)	−2068 (3)	3221 (6)	8519 (2)	95 (2)
C(13)	−1847 (3)	1508 (5)	8191 (2)	93 (2)
C(14)	−663 (3)	915 (5)	8089 (2)	74 (1)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

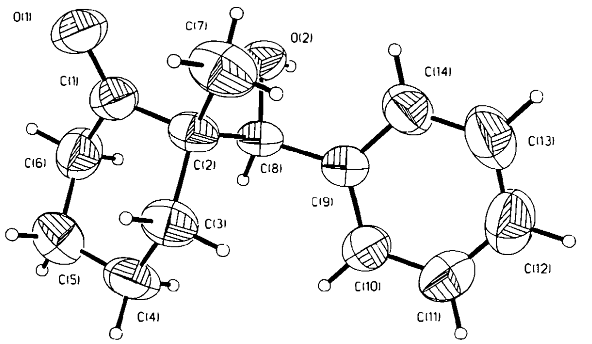

Fig. 1. Crystallographic asymmetric unit of (I).

Discussion. Final positional and isotropic thermal parameters for the non-H atoms are given in Table 1.* Fig. 1 shows a computer-generated plot with 50% thermal ellipsoids. The hydroxyl group is hydrogen bonded to the carbonyl O atom of an adjacent molecule generated by the symmetry transformation $0{\cdot}5 - x$, $0{\cdot}5 + y$, $1{\cdot}5 - z$. The O—O distance for this hydrogen bond is 2·79 (4) Å and the OH—O angle is 156·7 (3)°. No other unusual short intermolecular contacts were noted. It is interesting to note that the conformer observed in the solid state is less favorable on a unimolecular basis, since the more substituted hydroxy(phenyl)methyl side chain is in an axial position. On the basis of an *MM*2 calculation for an isolated molecule, the conformation depicted as (II) is favored by over 4 kJ mol^{-1}. In the solid state, internal hydrogen bonding is not possible in this molecule since the carbonyl O atom is eclipsed with the α-methyl substituent, *i.e.* 1·8 (4)° torsion angle for O(1)—C(1)—C(2)—C(7), and hence is directed away from hydroxyl group on C(8), *i.e.* the intramolecular O(1)—O(2) distance is 3·27 (7) Å in this conformation.

PGW acknowledges support for this research from the Biomedical Research Support Grant (BRSG) at Brown University. Funds for the purchase of the Nicolet crystallographic system were provided by the NSF through grant CHE-8206423.

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* Lists of structure factors, anisotropic thermal parameters, bond lengths and angles, torsion angles and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53468 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.