

non-hydrogen atoms are compiled in Tables 3 and 4. The five-membered ring is planar; the plane also includes the O and C atoms bonded to the ring. Deviations from the common least-squares plane are shown in Table 5. Corresponding bond distances are equal within experimental error. The S–N distances are characteristic for single bonds; the C–C distance within the ring shows partial double-bond character.

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## Structure of ( $\alpha R, 1R, 2R$ – $\alpha S, 1S, 2S$ )-1-Hydroxy- $\alpha$ -methyl-2-phenylcyclohexaneacetic Acid

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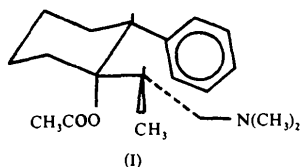
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**Abstract.** C<sub>15</sub>H<sub>20</sub>O<sub>3</sub>, m.p. 402–403 K, space group  $P2_1/a$ ,  $a = 11.389$  (3),  $b = 19.653$  (2),  $c = 5.892$  (1) Å,  $\beta = 92.76$  (2)°,  $Z = 4$ ,  $D_x = 1.252$ ,  $D_m$  (flotation: KI–H<sub>2</sub>O) = 1.25 Mg m<sup>-3</sup>. The structure was solved by *MULTAN*. Full-matrix least-squares refinement converged with  $R(F) = 0.04$ . The ( $\alpha R, 1R, 2R$ – $\alpha S, 1S, 2S$ ) stereochemistry confirms the *cis-threo* assignment of structure deduced earlier on the basis of PMR and chemical evidence.

**Introduction.** The synthesis of the ethyl ester of the title compound proceeds stereospecifically to give only one of four racemic diastereoisomers. Chemical and PMR data established the *cis* relationship of the phenyl and tertiary hydroxyl groups and led to the assignment of the *threo* stereochemistry about the acetate-to-ring bond (Thomas, Davidson, Griffith & Scott, 1976). Since this is a precursor of Nexeridine (I), an analgetic



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currently undergoing clinical trials, it was deemed advisable to confirm the structural assignments by single-crystal X-ray analysis.

Photographs of a crystal (from toluene) about 0.2 mm on an edge revealed monoclinic symmetry. Systematic absences and molecular asymmetry led to the assignment of space group  $P2_1/a$ . Lattice parameters were refined by least-squares fitting of 12 automatically centered reflections ( $32^\circ < 2\theta < 36^\circ$ ). Diffraction intensities were measured with Zr-filtered Mo  $K\alpha_1$  radiation ( $\lambda = 0.7093$  Å) on an automated Picker FACS-I diffractometer. Three standard reflections remained constant [ $\pm 2\sigma(I_{avg})$ ] throughout data collection. Of 1924 independent reflections ( $2\theta < 50^\circ$ ) of the form  $hkl$  and  $h\bar{k}l$  with respect to a right-handed crystal axial system, 444 were considered unobserved according to the criterion:  $|F_o| > 3.0\sigma$ . Integrated intensities were corrected for Lorentz and polarization effects but no absorption correction was applied. The structure was solved with *MULTAN* (Germain, Main & Woolfson, 1971). Normalized structure factors were calculated from the observed data and 200  $|E|$ 's ( $> 1.66$ ) were used to calculate a map which revealed the positions of all non-hydrogen atoms. Full-matrix least-squares refinement (Busing, Martin & Levy, 1962) with a  $1/\sigma^2$  weighting scheme, zerovalent

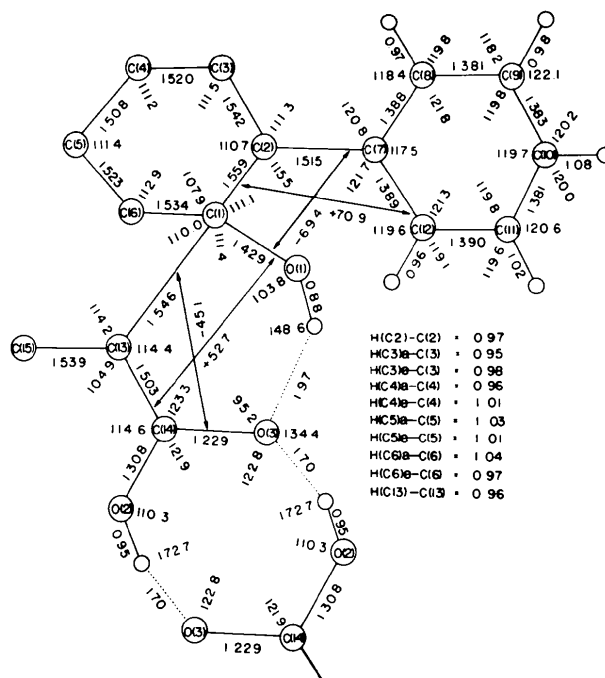
scattering factors, isotropic temperature factors and corrections for secondary extinction was followed by anisotropic refinement and calculation of a difference Fourier map. Of the 30 strongest peaks, 19 proved to be H atoms. The last H atom was located in a difference map generated in the final cycles of refinement accomplished in sections, first refining the heavier atoms and then the H atoms to which isotropic temperature factors of 5.0 Å<sup>2</sup> were initially assigned. Final parameter shifts were less than 0.5σ. The final residuals were  $R(F) = 0.040$  and  $R_w(F) = 0.052$ , minimizing  $\sum w(|F_o| - |F_c|)^2$ . Final atomic positional parameters are in Table 1.\*

\* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34574 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Positional parameters ( $\times 10^4$ , except for H  $\times 10^3$ ) for the title compound as fractions of the lattice translations

Estimated standard deviations in the last figures are given in parentheses. Anisotropic thermal parameters for atoms heavier than H and isotropic thermal parameters for H atoms have been deposited.

	x	y	z
O(1)	6881 (2)	6468 (1)	4305 (3)
O(2)	5909 (2)	5473 (1)	-1843 (3)
O(3)	5411 (2)	5630 (1)	1711 (3)
C(1)	7572 (2)	6484 (1)	2346 (4)
C(2)	8561 (2)	5935 (1)	2507 (5)
C(3)	9366 (2)	6044 (1)	4656 (5)
C(4)	9906 (3)	6751 (2)	4707 (6)
C(5)	8971 (3)	7294 (1)	4501 (5)
C(6)	8160 (2)	7186 (1)	2400 (5)
C(7)	8149 (2)	5204 (1)	2311 (4)
C(8)	8366 (2)	4819 (1)	402 (5)
C(9)	7976 (3)	4157 (1)	166 (6)
C(10)	7348 (3)	3863 (2)	1860 (6)
C(11)	7147 (3)	4227 (1)	3807 (6)
C(12)	7556 (2)	4891 (1)	4030 (5)
C(13)	6797 (2)	6402 (1)	136 (4)
C(14)	6001 (2)	5792 (1)	104 (5)
C(15)	5978 (3)	7009 (2)	-410 (6)
H(C2)	905	603	124
H(C3) <i>a</i>	890	597	593
H(C3) <i>e</i>	993	567	469
H(C4) <i>a</i>	1037	678	611
H(C4) <i>e</i>	1047	682	345
H(C5) <i>a</i>	846	729	590
H(C5) <i>e</i>	934	776	440
H(C6) <i>a</i>	863	725	95
H(C6) <i>e</i>	756	754	235
H(C8)	880	503	-80
H(C9)	815	391	-124
H(C10)	705	334	170
H(C11)	668	402	506
H(C12)	743	514	541
H(C13)	730	636	-113
H(C15-1)	645	741	-91
H(C15-2)	545	708	104
H(C15-3)	547	687	-171
H(O1)	863	114	600
H(O2)	539	510	-176



O(1)—C(1)—C(6)	+ 105.1	H(C5 <sub>B</sub> )—C(5)—H(C5 <sub>B</sub> )	+ 108.5
C(2)—C(1)—C(3)	+ 111.1	H(C5 <sub>B</sub> )—C(5)—C(4)	+ 110.3
H(C2)—C(2)—C(1)	+ 105.1	H(C5 <sub>B</sub> )—C(5)—C(6)	+ 108.4
H(C2)—C(2)—C(3)	+ 105.4	H(C6 <sub>B</sub> )—C(6)—C(5)	+ 109.6
H(C2)—C(2)—C(7)	+ 108.1	H(C6 <sub>B</sub> )—C(6)—C(1)	+ 109.4
H(C3 <sub>B</sub> )—C(3)—C(2)	+ 107.3	H(C6 <sub>B</sub> )—C(6)—H(C6 <sub>B</sub> )	+ 106.5
H(C3 <sub>B</sub> )—C(3)—C(4)	+ 111.5	H(C6 <sub>B</sub> )—C(6)—C(1)	+ 109.1
H(C3 <sub>B</sub> )—C(3)—H(C3 <sub>B</sub> )	+ 104.8	H(C6 <sub>B</sub> )—C(6)—C(5)	+ 109.1
H(C3 <sub>B</sub> )—C(3)—C(2)	+ 106.2	H(C13)—C(13)—C(1)	+ 109.0
H(C3 <sub>B</sub> )—C(3)—C(4)	+ 115.0	H(C13)—C(13)—C(14)	+ 107.5
H(C4 <sub>B</sub> )—C(4)—C(3)	+ 106.8	H(C13)—C(13)—C(5)	+ 106.4
H(C4 <sub>B</sub> )—C(4)—C(5)	+ 111.9	H(C15-1)—C(15)—C(13)	+ 110.1
H(C4 <sub>B</sub> )—C(4)—H(C4 <sub>B</sub> )	+ 106.3	H(C15-1)—C(15)—H(C15-2)	+ 117.1
H(C4 <sub>B</sub> )—C(4)—C(3)	+ 111.8	H(C15-1)—C(15)—H(C15-3)	+ 107.0
H(C4 <sub>B</sub> )—C(4)—C(5)	+ 108.8	H(C15-2)—C(15)—C(13)	+ 107.0
H(C5 <sub>B</sub> )—C(5)—C(4)	+ 110.2	H(C15-2)—C(15)—H(C15-3)	+ 108.8
H(C5 <sub>B</sub> )—C(5)—C(6)	+ 108.0	H(C15-3)—C(15)—C(13)	+ 106.4

Fig. 1. Bond lengths (Å), bond angles (°), torsion angles (°) and intra- and intermolecular hydrogen-bonding distances and angles for ( $\alpha R,1R,2R-\alpha S,1S,2S$ )-1-hydroxy- $\alpha$ -methyl-2-phenylcyclohexaneacetic acid. Estimated standard deviations are 0.003 Å (C—C and C—O) and 0.05 Å (C—H and O—H) for bond lengths, 0.2° (C—C—O and O—C—O), 0.6° (C—C—H, C—O—H) and 1.0° (H—C—H and H—O...H) for bond angles and 0.3° for the torsion angles.

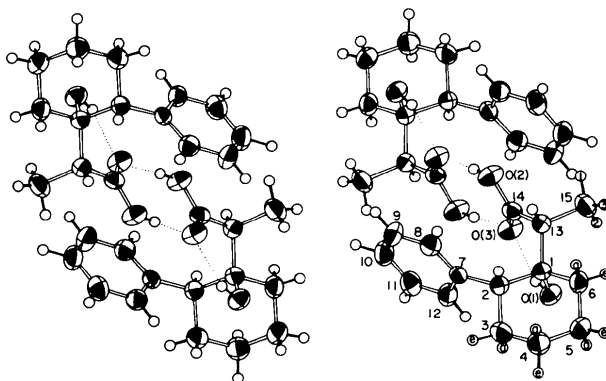


Fig. 2. Stereoprojection of ( $\alpha R,1R,2R-\alpha S,1S,2S$ )-1-hydroxy- $\alpha$ -methyl-2-phenylcyclohexaneacetic acid down the z axis. Atoms are represented by thermal ellipsoids including 50% probability. The broken lines represent hydrogen bonds.

**Discussion.** Bond lengths and angles (Fig. 1) are consistent with those observed in other related compounds (Hite & Craven, 1973; Hite & Soares, 1973; Ruble, Blackmond & Hite, 1976; Ruble, Hite & Soares, 1976*a,b*). The benzene ring is equatorial and *cis* to the tertiary hydroxyl group. The (*αR,1R,2R-αS,1S,2S*) stereochemistry of this racemate confirms the *cis-threo* assignment of structure made earlier on the basis of PMR and chemical data (Thomas, Davidson, Griffith & Scott, 1976). The tertiary hydroxyl groups are intramolecularly hydrogen bonded to the carbonyl O atoms (Figs. 1 and 2). Enantiomeric pairs of molecules are dimerized through head-to-tail hydrogen bonding to give classic, planar eight-membered rings which are nearly parallel to the planes of the aromatic rings. These conformational features are defined by the torsion angles shown in Fig. 1. The hydrophilic groups are sandwiched between the hydrophobic aromatic rings of the dimers. There are no other hydrogen bonds. Thus, the dimeric units are held together in the lattice by ring stacking approximately along the *z* axis, by

other interactions and possibly by long-range dipolar interactions. All intermolecular C...C distances are greater than 3.82 Å.

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### 3,4,6,8β,9,10-Hexamethyltetracyclo[4.3.1.0<sup>3,10</sup>.0<sup>4,9</sup>]decane-2,5-dione

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**Abstract.** C<sub>16</sub>H<sub>22</sub>O<sub>2</sub>, triclinic, *P* $\bar{1}$ , *a* = 7.7672 (10), *b* = 8.7689 (6), *c* = 10.3545 (6) Å, *α* = 85.589 (5), *β* = 76.909 (7), *γ* = 89.228 (7)°, *Z* = 2, *D<sub>x</sub>* = 1.19 Mg m<sup>-3</sup>, *μ*(Cu *Kα*) = 0.568 mm<sup>-1</sup>; *R* = 0.042 for 2487 reflexions. This novel tetracyclic solution photo-product is completely different from that obtained in the solid state and bears little resemblance to the 1,4-naphthoquinone derivative from which it is formed. The crystal structure consists of discrete molecular units with bond distances and angles which suggest a highly strained system.

**Introduction.** Recrystallization from CCl<sub>4</sub> afforded large colourless chunks from which a fragment of dimensions *ca* 0.2 × 0.3 × 0.4 mm was cut. A series of precession photographs provided an initial unit cell and the Laue symmetry  $\bar{1}$ . Accurate unit-cell parameters were determined by least-squares analysis of the setting angles of 25 reflections (70 < *θ* < 75°, Ni-filtered Cu *Kα* radiation) automatically located and centred on an Enraf–Nonius CAD-4 diffractometer. The intensities

were collected with an *ω*–2*θ* scan, *Δω* = (1.0 + 0.15 tan *θ*)°, an aperture 4 mm high and (1.5 + 0.5 tan *θ*) mm wide, a pre-scan acceptance limit of 6*σ* at 5.03° min<sup>-1</sup> and a maximum recording time of 180 s. Of 2822 recorded intensities out to *θ* = 75°, 2487 (88%) had *I/σ(I)* ≥ 3 with *σ*<sup>2</sup>(*I*) = *S* + *B* + (0.04*S*)<sup>2</sup> (*S* being the scan and *B* the background count). During the data collection three standard reflections were checked periodically and their intensities showed a steady decrease to 96% of their initial value; this was corrected for during data processing where Lorentz and polarization corrections were applied. Absorption correction using a Gaussian integration method gave transmission factors for *I* varying between 0.769 (930) and 0.914 (011).

All non-hydrogen atoms were located by direct methods; the *|E|* statistics clearly indicated the centrosymmetric space group. With all atoms refined as C in isotropic full-matrix least squares, the O atoms were clearly identified by their abnormally low thermal parameters.