

## Molecular and crystal structure of 1-hydroxy-2-methyl-11-methylene-tricyclo (5.3.1.0)<sup>2,7</sup>-undecan-5-one, C<sub>13</sub>O<sub>2</sub>H<sub>18</sub>

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**Abstract.** The title compound is orthorhombic with  $a = 26.132(6)$ ,  $b = 11.023(2)$ ,  $c = 8.317(5)$ , Å; space group  $Iba2$ ;  $Z = 8$ ,  $D_m = 1.21(1)$ ,  $D_c = 1.192 \text{ Mg m}^{-3}$ ,  $\frac{1}{2}(\text{H}_2\text{O})$  per molecule in asymmetric unit;  $\lambda (\text{MoK}\alpha) = 0.7107 \text{ \AA}$ ;  $\mu = 0.46 \text{ cm}^{-1}$ ;  $F(000) = 936$ . The structure was solved by direct methods and refined to  $R(F)$  value of 0.069 using 327 reflections with  $F \geq 5\sigma(F)$  out of 727 independent reflections for  $2\theta \text{ max} = 46^\circ$ . The *trans* fused cyclohexane and cyclohexanone rings form layers along the  $a$ - $b$  plane. The axial methyl attached at the bridge-head, interlocks with the translated methylene of the cyclobutane fused across the cyclohexane ring. The equatorial hydroxyl at the bridge-head adjacent to the methyl junction and the water molecule on the two-fold form a water bridge along the  $z$  axis. The packing is reminiscent of that observed for the cholesterol used in membrane structure studies.

**Keywords.** X-ray structure; tricyclic; cyclobutane; cholesterol packing.

### 1. Introduction

The title compound was obtained through an unusual reductive cyclisation (Kannan *et al* 1984) (figure 1). Such a cyclisation, leading to the formation of a cyclobutane ring in metal ammonia reactions, had not been reported earlier. The X-ray structure determination of this compound was taken up primarily to verify the difficult cyclisation and the structure proposed by chemists using <sup>13</sup>C NMR evidence. The X-ray structure confirms the proposed structure (figure 2). An interesting feature that emerges from the structure solution is the tendency of this rigid tricyclic alcohol to mimic the crystal packing of cholesterol, in terms of interlocking of the projecting groups and alternation of hydrophobic and hydrophilic layers.

### 2. Experimental

The compound in the form of crystals was supplied courtesy Prof. S Swaminathan, Organic Chemistry, University of Madras. Accurate unit cell dimensions were obtained by least squares fit of 25 reflections with  $10 \leq \theta \leq 15^\circ$ , measured on an Enraf Nonius CAD4 Diffractometer using  $\text{MoK}\alpha$  radiation. The intensity data were corrected for Lorentz and polarisation effects. No absorption correction was

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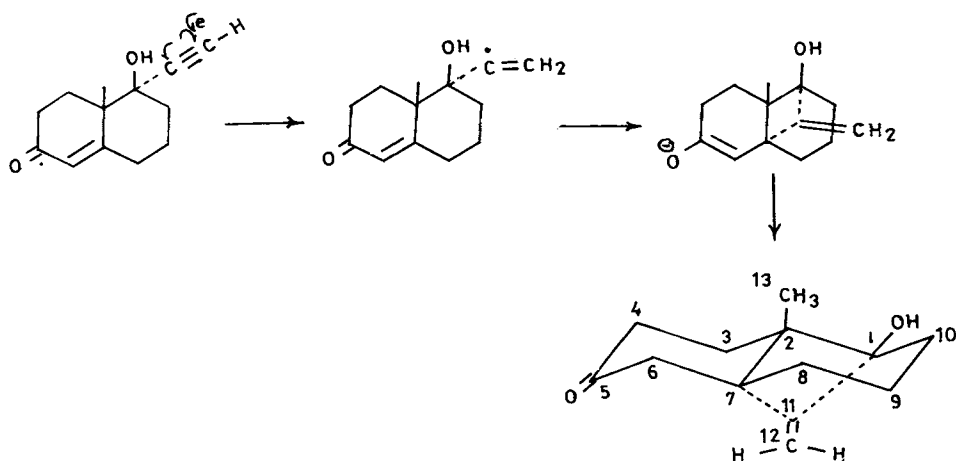


Figure 1. Schematic diagram of molecule and reduction scheme.

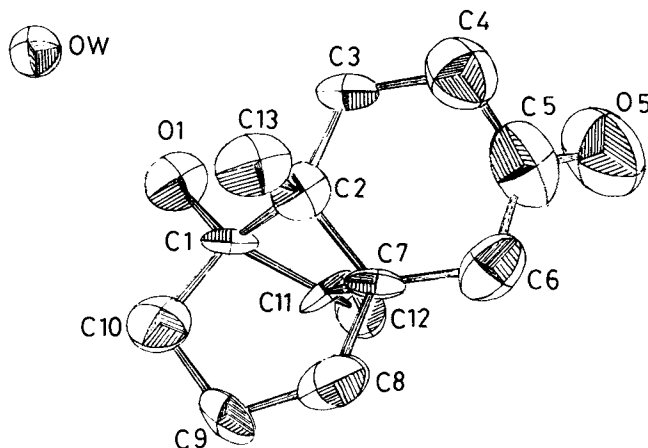


Figure 2. ORTEP diagram (Johnson 1965) showing thermal ellipsoids at 50% probability level.

applied. In the total of 727 reflections for  $2\theta$  max of  $46^\circ$ , 463 reflections had  $F \geq 3\sigma(F)$  and 327 reflections had  $F \geq 5\sigma(F)$ . The results appertaining to the crystal and the data collection are listed in table 1.

### 3. Structure solution and refinement

The space group *Iba*2 was assigned based on the non-centric distribution of the E statistics. The structure was solved using a direct method and the Karle recycling procedure through the program MULTAN 80 (Main *et al* 1980). Initially the data beyond  $3\sigma(F)$  limit were used for refinement. The *z* coordinate of the atom C(1) was held constant for fixing the origin on the two-fold axis. Block diagonal

**Table 1.** Crystal data.

Formula	$C_{13}O_2H_{18}\frac{1}{2}H_2O$	$Mr = 215.29$
System	orthorhombic	Space group <i>Iba2</i>
$a$	$= 26.132(6)$	$b = 11.023(2)$
$D_m$	$= 1.21(1)$	$D_c = 1.192 \text{ Mg m}^{-3}$
$\lambda(MoK\alpha)$	$= 0.7107 \text{ \AA}$	$Z = 8$
Crystal size	$0.4 \times 0.13 \times 0.08 \text{ mm}$	$F(000) = 926e$
$\frac{\sin \theta \max}{\lambda}$	$0.55 \text{ \AA}^{-1}$	$\mu = 0.46 \text{ cm}^{-1}$
Total hkl	727	
$F \geq 5\sigma(F)$	327	
$R$	0.069	

**Table 2.** Fractional coordinates ( $\times 10^4$ ) and equivalent thermal parameters ( $\times 10^4$ ) for non-hydrogen atoms. e.s.d. values in parentheses.

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

Atom	X	Y	Z	$U_{eq} (\text{\AA}^2)$
C1	9250 (5)	2208 (11)	-653 (19)	386 (31)
C2	8796 (5)	2001 (12)	478 (15)	527 (34)
C3	8538 (5)	802 (9)	210 (18)	505 (32)
C4	7969 (6)	839 (16)	449 (21)	957 (37)
C5	7741 (6)	1768 (16)	-645 (22)	900 (37)
C6	7946 (5)	3004 (13)	-587 (19)	666 (34)
C7	8516 (5)	3017 (10)	-483 (17)	406 (33)
C8	8721 (6)	4276 (12)	50 (20)	737 (37)
C9	9292 (6)	4449 (12)	-182 (16)	572 (36)
C10	9601 (5)	3234 (14)	-204 (18)	639 (35)
C11	8865 (5)	2648 (10)	-1859 (19)	376 (33)
C12	8794 (5)	2541 (14)	-3458 (18)	598 (35)
C13	8887 (5)	2157 (14)	2299 (16)	627 (36)
O1	9554 (4)	1174 (8)	-1131 (15)	675 (29)
O5	7379 (4)	1483 (11)	-1552 (18)	1341 (35)
				$U_{iso} (\text{\AA}^2)$
OW	10000	0	1401 (17)	518 (33)

refinement (Shiono 1968) with isotropic temperature factors converged at  $R = 0.15$ . The anisotropic temperature factor of C(1) was nonpositive definite. The water oxygen was treated isotropically. The clamp on the  $z$  coordinate of C(1) was shifted to the centre of mass of the molecule and the refinement was restarted. However the anisotropic temperature factors of C(2), C(3) and C(7) were nonpositive definite. The quality of the data prompted the use of a higher cut off, namely  $5\sigma(F)$ . The refinement was restarted from the Karle output stage. Isotropic refinement converged at  $R = 0.122$ . Anisotropic refinement converged at  $R = 0.106$  and the anisotropic temperature factors were normal. The hydrogens were fixed stereochemically. The water and hydroxyl hydrogens were not included. The  $R$  factor with the inclusion of the contribution of the hydrogens was 0.105. The hydrogens were not refined. As the bond lengths and estimated standard deviations at this stage were not reasonable the refinement was continued in the full matrix

procedure in SHELX 76 (Sheldrick 1976). A few cycles of refinement brought the  $R$  index to 0.08. At this stage 20 reflections had a  $F(\text{obs})/F(\text{calc})$  ratio of 1.5. Six of these, (3,1,0), (1,1,0), (28,2,0), (21,7,0), (22,0,2) and (7,1,2), which had a bad intensity profile in the data collection, were removed. A few cycles of damped refinement resulted in  $R = 0.069$ . On further refinement the anisotropic temperature factors of C(1), C(4) and C(11) were nonpositive definite. The refinement was terminated at  $R = 0.069$  as no further improvement of the geometry was expected with the present data set. The maximum shift to esd ratio in the parameters was 0.3. The difference map had no peak greater than  $0.25\text{e}\text{\AA}^{-3}$ . The weighted  $R$  was 0.055 with  $w = 3.003/\sigma^2(F)$  ( $0.0002F^2$ ) and the goodness of fit  $S = 2.78$ .

#### 4. Results and discussions

The coordinates, bond lengths and bond angles involving the non-hydrogen atoms are listed in tables 2 to 4. The cyclohexane ring is in the sofa form with C(2)

**Table 3.** Bond lengths ( $\text{\AA}$ ) involving non-hydrogen atoms. e.s.d. values in parentheses.

Atoms	Distance	Atoms	Distance
C1–C2	1.53 (2)	C5–C6	1.47 (2)
C1–C10	1.50 (2)	C5–O5	1.25 (2)
C1–C11	1.50 (2)	C6–C7	1.49 (2)
C1–O1	1.45 (2)	C7–C8	1.55 (2)
C2–C3	1.50 (2)	C7–C11	1.52 (2)
C2–C7	1.56 (2)	C8–C9	1.52 (2)
C2–C13	1.54 (2)	C9–C10	1.56 (2)
C3–C4	1.50 (2)	C11–C12	1.35 (2)
C4–C5	1.49 (2)		

**Table 4.** Bond angles ( $^\circ$ ) involving non-hydrogens e.s.d. values in parentheses.

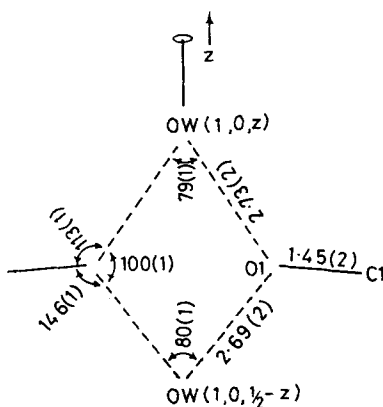
Atoms	Angle	Atoms	Angle
C2–C1–C10	116 (1)	C4–C5–O5	120 (2)
C2–C1–C11	87 (1)	C6–C5–O5	122 (2)
C2–C1–O1	119 (1)	C5–C6–C7	112 (1)
C10–C1–C11	109 (1)	C2–C7–C6	119 (1)
C10–C1–O1	109 (1)	C2–C7–C8	110 (1)
C11–C1–O1	116 (1)	C2–C7–C11	85 (1)
C1–C2–C3	113 (1)	C6–C7–C8	112 (1)
C1–C2–C7	87 (1)	C6–C7–C11	124 (1)
C1–C2–C13	118 (1)	C8–C7–C11	104 (1)
C3–C2–C7	110 (1)	C7–C8–C9	115 (1)
C3–C2–C13	108 (1)	C8–C9–C10	114 (1)
C7–C2–C13	120 (1)	C1–C10–C9	109 (1)
C2–C3–C4	114 (1)	C1–C11–C7	89 (1)
C3–C4–C5	110 (1)	C1–C11–C12	136 (1)
C4–C5–C6	118 (1)	C7–C11–C12	133 (1)

puckered. The C(9) end is flattened to accommodate the cyclobutane ring. The cyclobutane ring is puckered with a dihedral angle of  $38(1)^\circ$  between the planes through the atoms C(1), C(2), C(7) and C(1), C(11), C(7). The cyclohexanone ring is in the favoured chair form with puckering at C(2) and C(5). The torsion angles involving the rings are given in table 5. The bond angles and lengths within the rings are in agreement with the standard values expected for  $C(sp^3)-C(sp^3)$ , within experimental error (Eliel *et al* 1967; Allen 1984). The hydroxyl oxygen O(1) is equatorial, whereas the methyl C(13) and the cyclobutane forming C(11) are axial with respect to the cyclohexane ring.

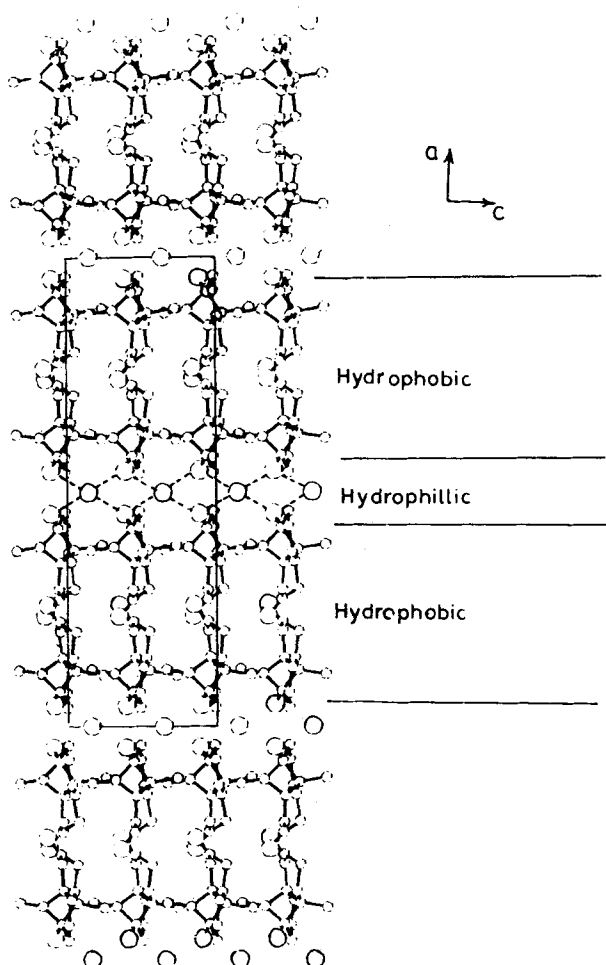
The hydrogen bonding and packing features are shown in figures 3 and 4. The methyl and methylene groups are nearly at right angles to the decalin-like ring

**Table 5.** Selected torsion angles ( $^\circ$ ) involving the ring atoms. e.s.d. values are given in parentheses.

<i>Cyclohexane</i>	
C1-C2-C7-C8	-77 (1)
C2-C7-C8-C9	59 (1)
C7-C8-C9-C10	-24 (2)
C8-C9-C10-C1	23 (2)
C9-C10-C1-C2	-60 (1)
C10-C1-C2-C7	83 (1)
<i>Cyclohexanone</i>	
C2-C3-C4-C5	57 (2)
C3-C4-C5-C6	-54 (2)
C4-C5-C6-C7	42 (2)
C5-C6-C7-C2	-34 (2)
C6-C7-C2-C3	39 (2)
C7-C2-C3-C4	-50 (1)
<i>Cyclobutane</i>	
C1-C2-C7-C11	26 (1)
C2-C7-C11-C1	-27 (1)
C7-C11-C1-C2	27 (1)
C11-C1-C2-C7	-26 (1)



**Figure 3.** Hydrogen bonding features.



**Figure 4.** Packing diagram down  $b$  axis showing the water bridge and the alternate hydrophobic and hydrophilic layers. The methyl-methylene interlocking can also be seen.

system. These ring systems along the  $a$ - $b$  plane are interlocked by the methyl and the methylene groups ( $C(13)\dots C(12)$  ( $x, y, z + 1$ ):  $3.56\text{\AA}$ ). The packing of cholesteryl myristate (Craven and De Titta 1976) shows similar methyl interlocking involving the axial methyls of the steroid rings. Likewise, the alternate hydrophilic and hydrophobic layers seen in figure 4, are similar to the packing of the cholesterol monohydrate structure (Craven 1976).

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