

*Acta Cryst.* (1973). B29, 2642**5-Hydroxy-2,3-norbornane Dicarboxylic Acid  $\gamma$ -Lactone\***

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**Abstract.** C<sub>9</sub>H<sub>10</sub>O<sub>4</sub>, monoclinic,  $P2_1/n$ ;  $a=22.421$  (8),  $b=6.685$  (2),  $c=10.914$  (4) Å,  $\beta=94.34$  (5)°,  $Z=8$ ,  $D_x=1.483$  (5),  $D_m=1.47$  (1) g cm<sup>-3</sup>. The two molecules of the asymmetric unit are hydrogen bonded to each other through their carboxyl groups, and form a pseudocentric dimer. The dimensions of two molecules are identical within the statistical accuracy.

**Introduction.** Recently Koshland and coworkers (1971) stressed the importance of orientation factors to chemical reaction velocities with special reference to the catalytic power of enzymes. To explore this hypothesis, they studied the relative velocities of some intramolecular lactonizations, using norbornane derivatives which provide a rigid geometrical frame (Storm & Koshland, 1972). This crystallographic study was undertaken for one of these compounds to obtain an accurate description of its molecular geometry. The

crystals were kindly supplied to us by Professor D. E. Koshland and D. Hackney.

A preliminary photographic study of a crystal with dimensions 0.2 × 0.5 × 0.7 mm showed the Laue symmetry  $2/m$  and the diffracting conditions  $h+l=2n$  for  $h0l$  and  $k=2n$  for  $0k0$  reflections, leading to space group  $P2_1/n$ . Lattice parameters were determined by a least-squares refinement of the setting angles of 12 reflections within the range  $40^\circ \leq 2\theta \leq 44^\circ$ ; the temperature was  $\approx 23^\circ$ . The intensities were measured with an automatic Picker FACS I diffractometer, graphite-monochromatized Mo  $K\alpha$  radiation ( $\lambda=0.70926$  Å) and a  $\theta$ - $2\theta$  scan technique. One half of the reciprocal sphere was measured in the range  $3^\circ \leq 2\theta \leq 45^\circ$ . 2143 unique reflections were obtained, of which 1667 with  $I > \sigma(I)$  were used for the least-squares refinements. Absorption was small,  $\mu_{\text{Mo } K\alpha}=0.73$  cm<sup>-1</sup>, and no correction was necessary. The crystal structure was solved by direct methods with the *MULTAN* program (Germain, Main & Woolfson, 1971) and refined by our full-matrix least-squares program. The final

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Table 1. Atomic parameters

Estimated standard deviations of the least significant digits are indicated in parentheses. The thermal parameters are in units of Å<sup>2</sup>. The temperature factor is  $\exp(-T)$ , where  $T = -\frac{1}{4} \sum h_i h_j B_{ij} a_i^* a_j^*$  for the anisotropic case and  $T = -B \sin^2 \theta / \lambda^2$  for the isotropic case.

	$x$	$y$	$z$	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$
C(1)	0.3341 (1)	0.2473 (4)	0.1160 (2)	2.6 (1)	3.4 (1)	3.6 (1)	-0.4 (1)	0.6 (1)	0.3 (1)
C(2)	0.3444 (1)	0.4689 (4)	0.1521 (2)	2.7 (1)	3.7 (1)	2.1 (1)	0.4 (1)	0.64 (9)	0.1 (1)
C(3)	0.4130 (1)	0.4954 (4)	0.1365 (2)	2.6 (1)	3.0 (1)	2.2 (1)	-0.04 (9)	0.03 (9)	-0.17 (9)
C(4)	0.4335 (1)	0.2774 (4)	0.1255 (2)	2.2 (1)	3.6 (1)	2.8 (1)	0.5 (1)	-0.12 (9)	0.29 (9)
C(5)	0.4164 (1)	0.2503 (4)	-0.0114 (2)	3.3 (1)	2.8 (1)	2.8 (1)	0.5 (1)	0.5 (1)	-0.0 (1)
C(6)	0.3491 (1)	0.2076 (5)	-0.0160 (2)	3.3 (1)	3.4 (1)	3.5 (1)	-0.3 (1)	-0.3 (1)	-0.4 (1)
C(7)	0.3880 (1)	0.1516 (5)	0.1871 (3)	4.1 (2)	3.5 (2)	2.9 (1)	0.3 (1)	0.5 (1)	0.5 (1)
C(8)	0.3041 (1)	0.6165 (4)	0.0848 (2)	2.2 (1)	3.3 (1)	3.0 (1)	0.08 (9)	0.5 (1)	-0.2 (1)
C(9)	0.4256 (1)	0.5873 (4)	0.0162 (2)	2.0 (1)	3.1 (1)	3.2 (1)	0.6 (1)	0.35 (9)	0.2 (1)
C(10)	0.1628 (1)	0.3509 (4)	0.8748 (2)	2.9 (1)	3.8 (2)	3.6 (1)	-0.2 (1)	0.8 (1)	0.3 (1)
C(11)	0.1511 (1)	0.1274 (4)	0.8453 (2)	2.9 (1)	3.9 (1)	2.0 (1)	0.3 (1)	0.47 (9)	-0.2 (1)
C(12)	0.0836 (1)	0.1046 (4)	0.8694 (2)	2.2 (1)	3.4 (1)	2.7 (1)	-0.1 (1)	-0.47 (9)	-0.4 (1)
C(13)	0.0637 (1)	0.3230 (4)	0.8791 (2)	2.5 (1)	3.5 (1)	2.7 (1)	0.7 (1)	-0.10 (9)	0.1 (1)
C(14)	0.0854 (1)	0.3583 (4)	1.0130 (2)	3.4 (1)	3.2 (1)	2.7 (1)	0.6 (1)	0.46 (9)	-0.0 (1)
C(15)	0.1521 (1)	0.3997 (5)	1.0081 (2)	3.4 (2)	3.1 (1)	3.8 (1)	-0.2 (1)	-0.4 (1)	-0.4 (1)
C(16)	0.1071 (1)	0.4424 (5)	0.8079 (3)	4.5 (2)	3.3 (2)	3.4 (1)	0.5 (1)	0.5 (1)	0.5 (1)
C(17)	0.1935 (1)	-0.0154 (4)	0.9124 (2)	2.2 (1)	3.5 (1)	3.0 (1)	-0.0 (1)	0.6 (1)	-0.5 (1)
C(18)	0.0743 (1)	0.0205 (5)	0.9941 (2)	2.0 (1)	3.6 (1)	3.8 (1)	-0.1 (1)	0.08 (9)	0.6 (1)
O(1)	0.27270 (9)	0.7245 (3)	0.1568 (2)	4.4 (1)	5.5 (1)	3.27 (9)	2.19 (9)	0.71 (8)	-0.30 (8)
O(2)	0.29959 (8)	0.6370 (3)	-0.0263 (2)	4.1 (1)	5.7 (1)	2.91 (9)	2.29 (8)	0.64 (7)	0.39 (7)
O(3)	0.42876 (7)	0.4420 (3)	-0.0690 (1)	3.52 (9)	3.40 (9)	2.56 (7)	0.25 (7)	0.75 (6)	0.36 (7)
O(4)	0.43294 (9)	0.7602 (3)	-0.0088 (2)	3.9 (1)	3.2 (1)	5.6 (1)	0.19 (8)	0.95 (7)	0.91 (8)
O(5)	0.22501 (9)	0.8777 (3)	0.8408 (2)	4.7 (1)	5.4 (1)	3.27 (9)	2.36 (9)	0.78 (8)	-0.23 (8)
O(6)	0.19862 (8)	-0.0322 (3)	1.0233 (2)	4.2 (1)	5.4 (1)	3.03 (9)	2.27 (8)	0.27 (7)	-0.15 (7)
O(7)	0.07498 (8)	0.1702 (3)	1.0762 (1)	3.46 (9)	4.7 (1)	2.70 (8)	0.24 (8)	0.72 (6)	0.43 (8)
O(8)	0.06579 (9)	-0.1500 (3)	1.0223 (2)	4.1 (1)	4.0 (1)	6.5 (1)	-0.48 (9)	0.45 (8)	1.85 (9)

Table 1 (cont.)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
H(1)	0.291 (1)	0.194 (3)	0.142 (2)	3.1 (5)
H(2)	0.338 (1)	0.479 (3)	0.246 (2)	2.4 (5)
H(3)	0.433 (1)	0.581 (3)	0.209 (2)	2.5 (5)
H(4)	0.477 (1)	0.250 (3)	0.150 (2)	2.6 (6)
H(5)	0.441 (1)	0.144 (3)	-0.057 (2)	2.1 (5)
H(6)	0.342 (1)	0.053 (4)	-0.037 (2)	3.4 (6)
H(7)	0.325 (1)	0.296 (4)	-0.085 (2)	4.3 (6)
H(8)	0.392 (1)	-0.002 (4)	0.169 (2)	4.1 (7)
H(9)	0.388 (1)	0.178 (3)	0.281 (2)	2.7 (5)
H(10)	0.243 (2)	0.814 (5)	0.100 (3)	6.2 (8)
H(11)	0.205 (1)	0.398 (4)	0.845 (2)	4.0 (6)
H(12)	0.1555 (9)	0.105 (3)	0.754 (2)	2.0 (5)
H(13)	0.062 (1)	0.017 (3)	0.801 (2)	2.2 (5)
H(14)	0.018 (1)	0.342 (3)	0.858 (2)	3.1 (6)
H(15)	0.062 (1)	0.470 (4)	1.060 (2)	3.0 (5)
H(15)	0.180 (1)	0.318 (4)	1.078 (2)	3.3 (5)
H(17)	0.158 (1)	0.554 (5)	1.024 (2)	4.6 (7)
H(18)	0.103 (1)	0.406 (4)	0.710 (2)	3.7 (6)
H(19)	0.105 (1)	0.600 (4)	0.825 (2)	2.8 (6)
H(20)	0.252 (1)	0.784 (4)	0.897 (3)	5.9 (8)

residual values obtained are  $R_1 = \sum |\Delta F| / \sum |F_o| = 0.042$  and  $R_2 = [\sum w |\Delta F|^2 / \sum w |F_o|^2]^{1/2} = 0.042$  where  $w = 1/\sigma^2(F)$  for all data with  $I > \sigma(I)$ , otherwise  $w = 0$ ; for all the data  $R_1 = 0.065$ . The scattering factors used for oxygen and carbon atoms are those tabulated by Doyle & Turner (1968). In the last stage of refinement the polar hydrogen model (Templeton, Olson, Zalkin & Templeton, 1972) was used in connection with the hydrogen

Table 2. Bond lengths (Å)

Molecule 1		Molecule 2	
C(1)-C(2)	1.546 (4)	C(10)-C(11)	1.547 (3)
C(1)-C(6)	1.528 (3)	C(10)-C(15)	1.528 (3)
C(1)-C(7)	1.528 (4)	C(10)-C(16)	1.528 (4)
C(2)-C(3)	1.569 (3)	C(11)-C(12)	1.564 (3)
C(2)-C(8)	1.493 (3)	C(11)-C(17)	1.498 (3)
C(3)-C(4)	1.537 (3)	C(12)-C(13)	1.533 (3)
C(3)-C(9)	1.496 (3)	C(12)-C(18)	1.501 (3)
C(4)-C(5)	1.525 (3)	C(13)-C(14)	1.524 (3)
C(4)-C(7)	1.519 (4)	C(13)-C(16)	1.518 (4)
C(5)-C(6)	1.533 (4)	C(14)-C(15)	1.525 (4)
O(1)-C(8)	1.311 (3)	O(5)-C(17)	1.305 (3)
O(2)-C(8)	1.217 (2)	O(6)-C(17)	1.213 (3)
O(3)-C(5)	1.463 (3)	O(7)-C(14)	1.462 (3)
O(3)-C(9)	1.350 (3)	O(7)-C(18)	1.342 (3)
O(4)-C(9)	1.202 (3)	O(8)-C(18)	1.200 (3)
C(1)-H(1)	1.09 (2)	C(10)-H(11)	1.06 (3)
C(2)-H(2)	1.05 (2)	C(11)-H(12)	1.02 (2)
C(3)-H(3)	1.05 (2)	C(12)-H(13)	1.03 (2)
C(4)-H(4)	1.01 (2)	C(13)-H(14)	1.03 (2)
C(5)-H(5)	1.05 (2)	C(14)-H(15)	1.06 (2)
C(6)-H(6)	1.07 (3)	C(15)-H(16)	1.10 (2)
C(6)-H(7)	1.07 (2)	C(15)-H(17)	1.05 (3)
C(7)-H(8)	1.05 (3)	C(16)-H(18)	1.09 (2)
C(7)-H(9)	1.04 (2)	C(16)-H(19)	1.07 (2)
O(1)-H(10)	1.06 (3)	O(5)-H(20)	1.04 (3)
O(1)···O(6)	2.676 (3)		
O(2)···O(5)	2.669 (3)		
O(2)···H(20)	1.63 (3)		
O(6)···H(10)	1.62 (3)		

scattering factor given by Stewart, Davidson & Simpson (1965).\*

**Discussion.** The final parameters are given in Table 1. The numbering of the atoms is given on the schematic diagram in Fig. 1. The two molecules in the asymmetric unit may be related by a non-crystallographic center of symmetry lying approximately at (0.25, 0.30, 0.50). The weak intensities of the reflections  $h0l$  for which  $h \neq 2n$  and  $l \neq 2n$  are a measure of the departure from a

\* A table of structure factors has been deposited with the National Lending Library, England, as Supplementary Publication No. SUP 30179 (11 pp.). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1 NZ, England.

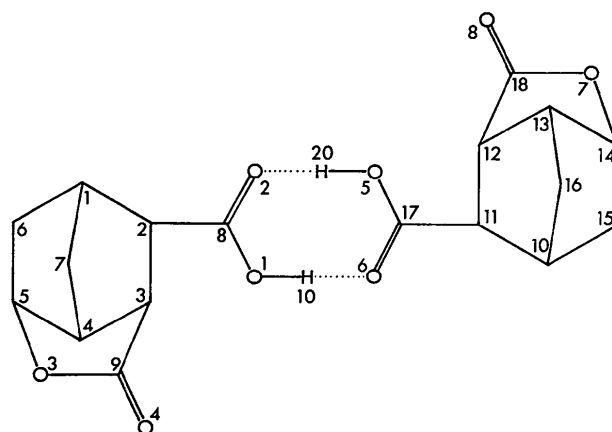


Fig. 1. Schematic diagram of the two molecules.

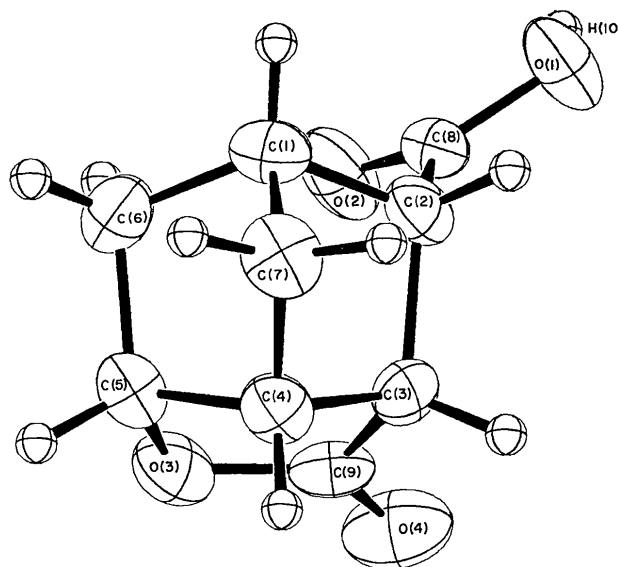


Fig. 2. Perspective view of one molecule with 50% probability thermal ellipsoids. For hydrogen atoms an arbitrary temperature parameter of  $1.0 \text{ \AA}^2$  was given.

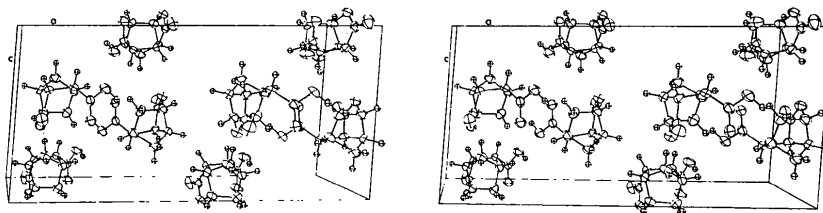


Fig. 3. Stereoscopic view of the crystal structure along the monoclinic  $b$  axis.

true center of symmetry. This center was also evident by the hypercentric-like distribution of the Wilson plot (Lipson & Woolfson, 1952).

Tables 2 and 3 give the bond distances and angles. The crystal consists of hydrogen-bonded dimers where one molecule is related to the other by the non-crystallographic center of symmetry. Owing to the strains in the norbornane molecules, the C-C bonds and angles depart significantly from the average values. The short C-C bonds C(2)-C(8), C(3)-C(9), C(11)-C(17), C(12)-C(18) are due to a delocalization of unsaturation from the carbonyl groups. The bond angles C(1)-C(7)-C(4) [C(10)-C(16)-C(13) for the

second molecule] and C(3)-C(4)-C(5) [C(12)-C(13)-C(14)] are characteristic of norbornane derivatives and agree with the previously known norbornane derivatives (Filippini, Gramaccioli, Rovere & Simonetta, 1972; Flippen, 1972). Figs. 2 and 3 show the molecular conformation and packing. A statistical comparison of the interatomic distances of the two molecules by a probability plot (Hamilton & Abrahams, 1972) yielded a slope of 1.0 which indicates that the two molecules have identical dimensions within the accuracy of the determination.

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Table 3. Bond angles ( $^{\circ}$ )

Molecule 1		Molecule 2	
C(2)-C(1)-C(6)	111.6 (2)	C(11)-C(10)-C(15)	111.6 (2)
C(2)-C(1)-C(7)	100.0 (2)	C(11)-C(10)-C(16)	99.6 (2)
C(6)-C(1)-C(7)	100.6 (2)	C(15)-C(10)-C(16)	100.8 (2)
C(1)-C(2)-C(3)	102.1 (2)	C(10)-C(11)-C(12)	102.2 (2)
C(1)-C(2)-C(8)	115.7 (2)	C(10)-C(11)-C(17)	115.0 (2)
C(3)-C(2)-C(8)	115.7 (2)	C(12)-C(11)-C(17)	116.3 (2)
C(2)-C(3)-C(4)	101.8 (2)	C(11)-C(12)-C(13)	102.1 (2)
C(2)-C(3)-C(9)	113.2 (2)	C(11)-C(12)-C(18)	113.0 (2)
C(4)-C(3)-C(9)	104.1 (2)	C(13)-C(12)-C(18)	103.5 (2)
C(3)-C(4)-C(5)	97.7 (2)	C(12)-C(13)-C(14)	98.1 (2)
C(3)-C(4)-C(7)	105.9 (2)	C(12)-C(13)-C(16)	105.3 (2)
C(5)-C(4)-C(7)	103.9 (2)	C(14)-C(13)-C(16)	103.8 (2)
C(4)-C(5)-C(6)	103.2 (2)	C(13)-C(14)-C(15)	103.8 (2)
C(4)-C(5)-O(3)	106.0 (2)	C(13)-C(14)-O(7)	105.5 (2)
C(6)-C(5)-O(3)	111.5 (2)	C(15)-C(14)-O(7)	111.4 (2)
C(1)-C(6)-C(5)	102.9 (2)	C(10)-C(15)-C(14)	102.7 (2)
C(1)-C(6)-C(7)	94.3 (2)	C(10)-C(15)-C(13)	94.5 (2)
C(2)-C(8)-O(1)	113.6 (2)	C(11)-C(17)-O(5)	114.1 (2)
C(2)-C(8)-O(2)	124.5 (2)	C(11)-C(17)-O(6)	123.7 (2)
O(1)-C(8)-O(2)	121.9 (2)	O(5)-C(17)-O(6)	122.2 (2)
C(3)-C(9)-O(3)	109.4 (2)	C(12)-C(18)-O(7)	109.3 (2)
C(3)-C(9)-O(4)	129.2 (2)	C(12)-C(18)-O(8)	128.6 (2)
O(3)-C(9)-O(4)	121.4 (2)	O(7)-C(18)-O(8)	122.1 (2)

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