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The Crystal Structure of 7-*syn*-6-*endo*-Dehydroxybicyclo[2.2.1]heptane-2-*endo*-carboxylic Acid α-Lactone, $C_{10}H_{12}O_4$

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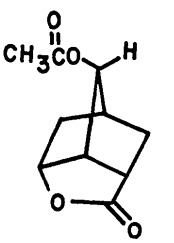
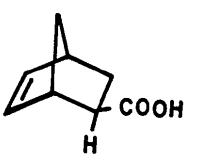
The crystal structure of 7-*syn*-6-*endo*-dehydroxybicyclo[2.2.1]heptane-2-*endo*-carboxylic acid α-lactone (acetoxylactone) has been determined. The molecule crystallizes in the space group $P2_1/c$ with $a=13{\cdot}810\pm0{\cdot}002$, $b=6{\cdot}206\pm0{\cdot}001$, $c=12{\cdot}555\pm0{\cdot}002$ Å, and $\beta=120{\cdot}4\pm0{\cdot}1°$. Data were collected on an automatic diffractometer. The structure was solved by the symbolic addition procedure and refined to a final R value of 0·051. The acetoxyl group is planar and *trans* to the lactone moiety. The molecules are held together by van der Waals forces.

The structure of acetoxylactone (I) formed by the lead tetraacetate oxidation of (II) was proven by chemical degradation (Moriarty, Gopal, Flippen & Karle, 1972). However the stereochemical relationship of the acetoxyl with respect to the lactone moiety group was not established. This stereochemical information is vital to the understanding of the mechanism by which (I) is formed and thus the X-ray study was undertaken.



(I)



(II)

The crystals used in the analysis were provided by Professor R. M. Moriarty of the University of Illinois. 1418 independent reflections were collected on a four-circle computer-controlled diffractometer using Cu $K\alpha$ radiation ($\lambda=1{\cdot}54178$ Å). The data were collected using the θ–2θ scanning technique. The space group is $P2_1/c$ with $a=13{\cdot}810\pm0{\cdot}002$, $b=6{\cdot}206\pm0{\cdot}001$, $c=12{\cdot}555\pm0{\cdot}002$ Å, and $\beta=120{\cdot}4\pm0{\cdot}1°$. There is one

Table 1. *Fractional coordinates* ($\times10^5$) *and thermal parameters* ($\times10^2$) *with standard deviations*

The thermal parameters are of the form $T=\exp[-\frac{1}{4}(B_{11}h^2a^{*2}+B_{22}k^2b^{*2}+B_{33}l^2c^{*2}+2B_{12}hka^*b^*+2B_{13}hla^*c^*+2B_{23}klb^*c^*)10^{-2}]$. The B_{ij}'s are in Å^2. The standard deviations are based solely on least-squares parameters. The hydrogen atom thermal parameters were not refined; each was assigned the thermal parameter of its adjoining atom.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	658 (18)	69376 (38)	36348 (20)	286 (9)	399 (11)	303 (9)	0 (7)	142 (7)	−4 (8)
C(2)	17800 (17)	55814 (41)	40829 (22)	252 (8)	446 (11)	363 (10)	−8 (7)	146 (8)	−125 (8)
C(3)	18997 (18)	80449 (40)	41089 (21)	280 (9)	441 (12)	293 (9)	−1 (7)	136 (7)	51 (8)
C(4)	29414 (18)	84935 (39)	53445 (21)	285 (9)	313 (10)	395 (10)	−20 (7)	158 (8)	−31 (8)
C(5)	26031 (18)	71154 (36)	61105 (20)	308 (9)	372 (10)	261 (9)	43 (7)	115 (8)	0 (7)
C(6)	14807 (19)	81802 (40)	57714 (21)	353 (10)	390 (11)	319 (10)	45 (8)	170 (8)	−42 (8)
C(7)	9362 (17)	86080 (38)	43480 (20)	276 (9)	295 (9)	336 (10)	28 (7)	129 (7)	26 (7)
C(8)	23866 (21)	49327 (37)	54495 (23)	356 (10)	289 (10)	442 (11)	28 (8)	212 (9)	4 (8)
C(9)	49205 (20)	83381 (45)	62724 (26)	288 (10)	465 (12)	505 (13)	−65 (8)	143 (9)	−70 (11)
C(10)	58705 (25)	73196 (65)	62316 (37)	324 (12)	636 (17)	707 (19)	−15 (11)	235 (12)	−61 (15)
O(1)	39177 (13)	77117 (28)	53270 (15)	255 (7)	428 (8)	419 (8)	−24 (5)	151 (6)	−60 (6)
O(2)	−9267 (13)	69723 (28)	32430 (15)	259 (7)	472 (9)	424 (8)	5 (5)	165 (6)	10 (6)
O(3)	5672 (13)	51905 (28)	34874 (15)	283 (7)	444 (8)	432 (8)	−48 (5)	148 (6)	−173 (6)
O(4)	50057 (18)	95672 (44)	70420 (24)	399 (9)	835 (14)	858 (14)	−108 (9)	178 (9)	−502 (12)
H(2)	2000 (25)	4844 (51)	3572 (30)						
H(3)	1857 (23)	8783 (53)	3408 (30)						
H(4)	3065 (24)	9993 (57)	5589 (28)						
H(5)	3125 (25)	7095 (50)	6935 (29)						
H(6*A*)	1620 (25)	9576 (56)	6199 (27)						
H(6*B*)	990 (25)	7285 (52)	5860 (27)						
H(7)	613 (24)	10074 (54)	4072 (28)						
H(8*A*)	1938 (26)	3997 (49)	5622 (28)						
H(8*B*)	3115 (28)	4197 (50)	5705 (28)						
H(10*A*)	5743 (29)	7228 (64)	5412 (43)						
H(10*B*)	6560 (30)	8131 (67)	6667 (37)						
H(10*C*)	5936 (30)	5861 (77)	6403 (38)						

Table 2. *Observed and calculated structure factors for* $C_{10}H_{12}O_4$

The columns are the index *l*, $|F_o| \times 10$ and $|F_c| \times 10$.

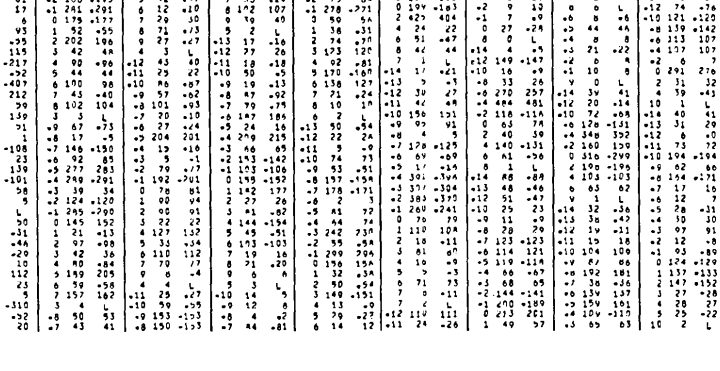
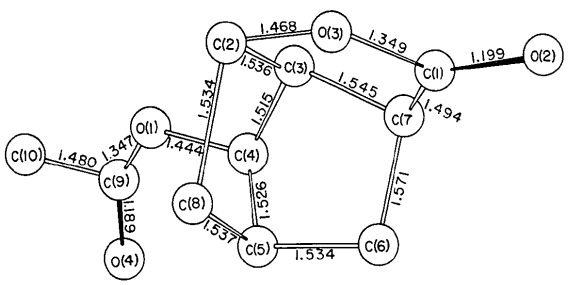
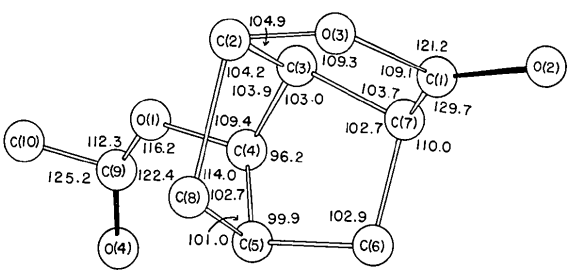


Fig. 1. Stereodiagram of the acetoxylactone molecule. The oxygen atoms are shown in black.

molecule per asymmetric unit corresponding to a crystallographic density of 1·40 g.cm^{-3}. The structure was solved using the symbolic addition procedure for centrosymmetric crystals (Karle & Karle, 1966). A computer program written by R. D. Gilardi of this laboratory was used to obtain a basic deck of phases and relationships between the symbols. The structure was refined using full-matrix least-squares methods. The function minimized was $\sum w(F_o-F_c)^2$ where $1/w=(|F_o|/10)^2+1{\cdot}0$. All the hydrogen atoms were located in a difference map and their positions were refined. No absorption corrections were made. The final R value for the full set of data was 0·051. Table 1 lists the atomic parameters and estimated standard deviations. Observed and calculated structure factors are compared in Table 2.

The stereoconfiguration of (I) is illustrated in Fig. 1. The acetoxyl group is planar (±0·001 Å) and is *trans* to the lactone moiety. The three five-membered rings in the bicyclic system are all in the envelope conformation. The six-membered ring [C(2), C(3), C(7), C(6), C(5), and C(8)] consists of two planes having atoms C(3) and C(5) in common. The dihedral angle between these planes is 72·0°. The bond distances and angles are illustrated in Fig. 2. The C(3)–C(4)–C(5) angle of 96·2±0·2° is small but characteristic for bicyclo-[2.2.1]heptyl derivatives (for example, MacDonald & Trotter, 1965; Fratini, Britts & Karle, 1967; Destro, Fillippini, Gramacciolo & Simonetta, 1969). The C(2)–C(3)–C(7) angle is also small, 97·8±0·2°, but not unexpectedly since it is in the bridging position of a bicyclo[3.2.1]octyl system. The molecules are held together by van der Waals forces. The packing is illustrated in Fig. 3. The molecules form interlocking chains such that the ester groups from neighboring chains face each other. The closest intermolecular approach between ester groups is C(9)–O(4′) at 3·13 Å. The lactone moieties from adjacent chains also face each other and the C=O bonds on the lactone are essentially parallel. The closest intermolecular approach here is C(1)–O(3′) at 3·09 Å.





O(3)-C(2)-C(8) 111.3
C(2)-C(3)-C(7) 97.8
C(6)-C(5)-C(8) 109.7

Fig. 2. Bonds distances and angles. Standard deviations (based solely on least-squares agreements) are of the order of 0·004 Å for the bonds and 0·2° for the angles. Bond distances were not corrected for thermal motion.

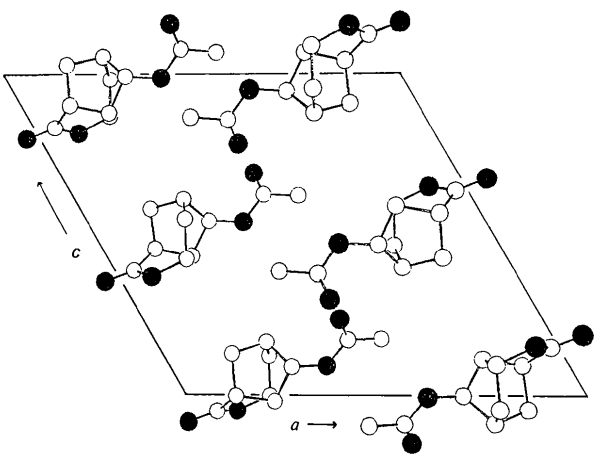


Fig. 3. Packing arrangement of acetoxylactone molecules seen looking approximately down the *b* axis. The oxygen atoms are shown in black. The figure was drawn using the *ORTEP* program of C. Johnson.

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