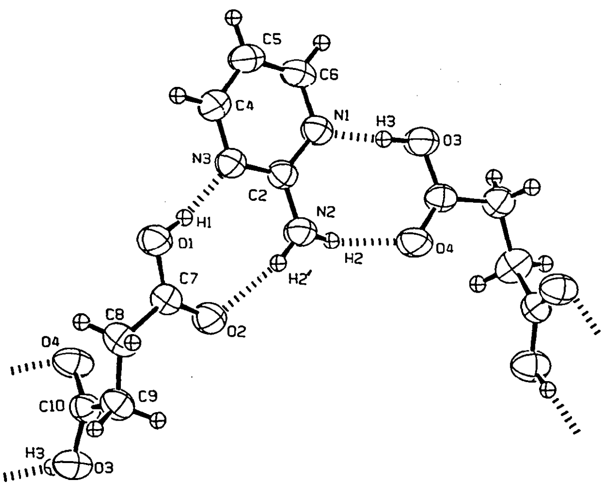

Fig. 1. *ORTEP* (Johnson, 1976) drawing (thermal ellipsoids, 50% probability level and H atoms of arbitrary size) of the hydrogen-bond pattern found in the 1:1 cocrystal of 2AP–SA. Dashed lines indicate hydrogen bonds. These three molecules are a portion of the hydrogen-bonded chain extended along the *b* axis.

in Table 1,* selected interatomic distances and angles are given in Table 2, and hydrogen-bond data in Table 3. The atomic numbering and hydrogen-bond scheme are shown in the *ORTEP* (Johnson, 1976) drawing in Fig. 1.

Related literature. 2-Aminopyrimidines typically associate *via* eight-membered hydrogen-bonded rings as seen in the crystal structures of 2-aminopyrimidine (Scheinbeim & Schempp, 1976), 2-amino-4,6-dichloropyrimidine (Clews & Cochran, 1948), and 2-amino-5-bromopyrimidine (Watton, Low, Tollin, & Howie, 1988). Succinic acid (Verweel & Macgillavry, 1939) forms typical carboxylic acid hydrogen-bonded rings. Adenine and 3-bromobenzoic acid cocrystallize to form an eight-membered hydrogen-bonded ring between the acid and aminopyrimidine moieties (Tamura, Sakurai, & Sato, 1971) similiar to the pattern in the 1:1 cocrystal of 2AP–SA described here.

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* Lists of structure factors, anisotropic thermal parameters, least-squares planes, H-atom parameters and intermolecular distances have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52517 (23 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Acta Cryst. (1990). **C46**, 934–936

Intramolecular Free-Radical Ring Closures. I. Structure of a Chiral Bicyclic Lactone*

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(*Received* 12 *July* 1989; *accepted* 17 *October* 1989)

Abstract. $C_{13}H_{18}O_6$, $M_r = 270{\cdot}28$, monoclinic, $P2_1$, $a = 6{\cdot}6619\,(3)$, $b = 10{\cdot}387\,(7)$, $c = 19{\cdot}895\,(2)$ Å, $\beta = 97{\cdot}33\,(4)°$, $V = 1356{\cdot}6$ Å^3, $Z = 4$, $D_x = 1{\cdot}323$ Mg m^{-3}, $\lambda(\text{Cu } K\alpha) = 1{\cdot}54178$ Å, $\mu = 0{\cdot}85$ mm^{-1}, $F(000) = 576$, $T = 296$ K, $R = 0{\cdot}039$ for 1812 observed reflections. A tin-mediated intramolecular radical cyclization of a chloromethyl ester afforded the title lactone in crystalline form. Although spectroscopic assignment of the reaction

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* Methyl (1*R*,2*S*,6*R*)-4,5-isopropylidenedioxy-8-oxo-*cis*-7-oxabicyclo[4.3.0]nonane-2-carboxylate.

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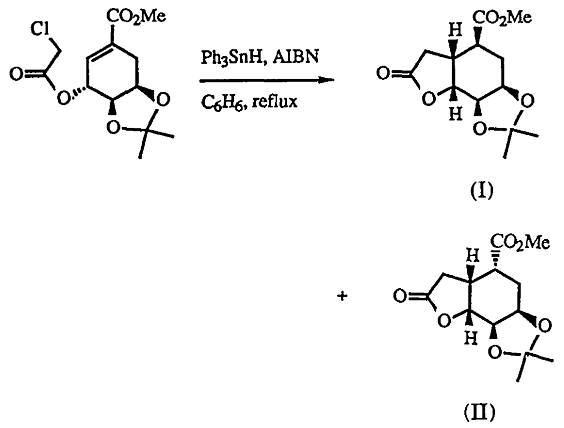
product based on ^{1}H NMR and nuclear Overhauser enhancement studies revealed the expected compound, X-ray analysis was used to give the definitive confirmation of the structure. The five-membered lactone is *cis* fused to a cyclohexane ring. The H atom α to the methyl ester carbonyl is *anti* to the ring-junction H atoms.

Experimental. The free-radical-induced cyclization shown below resulted in the formation of two bicyclic lactones (I) and (II) in 81·5% yield in a 6·2 : 1 ratio respectively. The crystalline isomer (I) was subjected to X-ray analysis.



A fragment from a crystal of (I), with size 0·29 × 0·61 × 0·12 mm from a large colorless trapezoidal plate, was mounted on an Enraf–Nonius CAD-4 diffractometer, Laue symmetry $2/m$ from 25 well centered reflections in the range $20 < \theta < 25°$. The space groups $P2_1$ and $P2_1/m$ were consistent with the systematic absences ($0k0$, $k \neq 2n$) identified in full data set. Graphite-monochromatized Cu *Kα* radiation was used, $2\theta_{\max} = 140°$. The data were collected in the ω-scan mode, $\Delta\omega = (1{\cdot}00 + 0{\cdot}14 \tan\theta)°$, at a scan speed of 4° min^{-1}. The orientation was checked every 200 measurements. The intensities of six standards (checked every hour) presented a maximum fluctuation of ±2·1%. 2153 reflections were measured, 1812 of which presented $I > 3\sigma(I)$. Data were corrected for Lp. h 0–7, k 0–11, l 0–±22.

Table 1. *Final atomic coordinates and their e.s.d.'s* (× 10^4) *and* $U_{\rm eq}$ *values* (Å^2 × 10^3) *for* $C_{13}H_{18}O_6$

$$U_{\rm eq} = (1/3)\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
C1*A*	5 (5)	7583	1909 (2)	62
O1*A*	−2785 (4)	6093 (3)	1755 (2)	93
C2*A*	195 (5)	7318 (5)	2662 (2)	81
O2*A*	−1436 (3)	6762 (3)	847 (1)	72
C3*A*	1326 (5)	8427 (5)	3049 (2)	74
O3*A*	2440 (4)	7980 (4)	3660 (1)	93
C4*A*	2998 (5)	9010 (4)	2669 (2)	67
O4*A*	4592 (4)	9343 (4)	3201 (1)	97
C5*A*	3769 (5)	8061 (4)	2189 (2)	63
O5*A*	5182 (3)	8737 (3)	1810 (1)	68
C6*A*	4464 (5)	8833 (4)	1150 (2)	63
O6*A*	5379 (4)	9396 (3)	766 (1)	81
C7*A*	2384 (5)	8222 (4)	1018 (2)	63
C8*A*	2118 (5)	7499 (3)	1663 (2)	62
C11*A*	−1541 (5)	6717 (4)	1507 (2)	68
C12*A*	−2933 (6)	6042 (5)	407 (2)	86
C14*A*	4145 (6)	8822 (6)	3823 (2)	98
C15*A*	5928 (8)	8064 (9)	4150 (2)	139
C16*A*	3557 (9)	9956 (8)	4251 (3)	139
C1*B*	4903 (5)	3439 (3)	2056 (2)	55
O1*B*	1407 (4)	4087 (3)	1764 (1)	74
C2*B*	4665 (5)	3433 (4)	2801 (2)	71
O2*B*	3295 (3)	3687 (3)	942 (1)	69
C3*B*	6797 (6)	3620 (4)	3171 (2)	69
O3*B*	6932 (4)	3286 (3)	3866 (1)	84
C4*B*	8392 (5)	2740 (4)	2898 (2)	64
O4*B*	9485 (4)	2195 (3)	3493 (1)	86
C5*B*	7438 (5)	1679 (4)	2441 (2)	63
O5*B*	9027 (4)	1029 (3)	2132 (1)	68
C6*B*	8963 (5)	1397 (4)	1478 (2)	66
O6*B*	10228 (4)	1030 (3)	1142 (1)	85
C7*B*	7192 (5)	2254 (4)	1275 (2)	63
C8*B*	5916 (5)	2180 (3)	1857 (2)	56
C11*B*	3013 (5)	3746 (3)	1589 (2)	58
C12*B*	1615 (6)	4039 (5)	439 (2)	76
C14*B*	9015 (6)	2892 (5)	4061 (2)	82
C15*B*	9083 (7)	2002 (7)	4661 (2)	108
C16*B*	10362 (8)	4040 (6)	4194 (2)	117

The structure was solved using *MULTAN*80,* refined on $|F_o|$ by full-matrix least squares. The asymmetric unit contained two symmetry-independent molecules labeled *A* and *B*. The refinement was anisotropic for C, O and isotropic for H atoms. The absolute configuration was deduced from the known chirality of asymmetric centers present in the starting material.

Final $R = 0{\cdot}039$, $wR = 0{\cdot}045$ {weights based on counting statistics, $w = 1/[\sigma^2(F) + 0{\cdot}00005F^2]$}, $S = 1{\cdot}37$; (shift/σ) mean 0·020, max. 0·05. The residual electron density fluctuation on final difference Fourier synthesis gave a general background ranging from −0·16 to 0·17 e Å^{-3}.

The scattering factors were taken from Cromer & Mann (1968) for O and C, and from Stewart, Davidson & Simpson (1965) for H.

Atomic parameters are given in Table 1, selected bond distances and angles in Table 2.* Fig. 1 shows a thermal-ellipsoid plot with the atom numbering.

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* The programs used here are modified versions of: *NRC*-2, data reduction, *NRC*-10, bond distances and angles and *NRC*-22, mean planes (Ahmed, Hall, Pippy & Huber, 1973); *FORDAP*, Fourier and Patterson maps (A. Zalkin, unpublished); *MULTAN*80, multisolution program (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); *NUCLS*, least-squares refinement (Doedens & Ibers, 1967); and *ORTEP* (Johnson, 1965).

* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, distances and angles involving the H atoms, torsion angles and a stereoview of the unit cell have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52338 (18 pp.). Copies may be obtained through the Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond distances* (Å) *and bond angles* (°) *with e.s.d.'s for* $C_{13}H_{18}O_6$

C1*A*—C2*A*	1·513 (5)	C1*B*—C2*B*	1·530 (5)
C1*A*—C8*A*	1·542 (5)	C1*B*—C8*B*	1·538 (5)
C1*A*—C11*A*	1·512 (5)	C1*B*—C11*B*	1·484 (5)
C2*A*—C3*A*	1·527 (6)	C2*B*—C3*B*	1·519 (5)
C3*A*—O3*A*	1·417 (4)	C3*B*—O3*B*	1·417 (4)
C3*A*—C4*A*	1·542 (5)	C3*B*—C4*B*	1·546 (5)
C4*A*—O4*A*	1·438 (4)	C4*B*—O4*B*	1·424 (4)
C4*A*—C5*A*	1·506 (5)	C4*B*—C5*B*	1·514 (5)
C5*A*—O5*A*	1·455 (4)	C5*B*—O5*B*	1·451 (4)
C5*A*—C8*A*	1·529 (5)	C5*B*—C5*B*	1·529 (5)
O5*A*—C6*A*	1·342 (2)	O5*B*—C6*B*	1·352 (4)
C6*A*—O6*A*	1·188 (5)	C6*B*—O6*B*	1·198 (5)
C6*A*—C7*A*	1·508 (5)	C6*B*—C7*B*	1·486 (5)
C7*A*—C8*A*	1·516 (5)	C7*B*—C8*B*	1·520 (5)
C11*A*—O1*A*	1·202 (5)	C11*B*—O1*B*	1·213 (4)
C11*A*—O2*A*	1·325 (5)	C11*B*—O2*B*	1·325 (4)
O2*A*—C12*A*	1·444 (5)	O2*B*—C12*B*	1·445 (4)
O3*A*—C14*A*	1·432 (6)	O3*B*—C14*B*	1·443 (5)
O4*A*—C14*A*	1·416 (5)	O4*B*—C14*B*	1·410 (5)
C14*A*—C15*A*	1·497 (8)	C14*B*—C15*B*	1·506 (7)
C14*A*—C16*A*	1·532 (9)	C14*B*—C16*B*	1·492 (8)
C2*A*—C1*A*—C8*A*	109·9 (3)	C2*B*—C1*B*—C8*B*	109·8 (3)
C2*A*—C1*A*—C11*A*	112·4 (3)	C2*B*—C1*B*—C11*B*	114·7 (3)
C8*A*—C1*A*—C11*A*	112·2 (3)	C8*B*—C1*B*—C11*B*	113·1 (3)
C1*A*—C2*A*—C3*A*	109·6 (3)	C1*B*—C2*B*—C3*B*	105·6 (3)
C2*A*—C3*A*—O3*A*	110·7 (3)	C2*B*—C3*B*—O3*B*	112·4 (3)
C2*A*—C3*A*—C4*A*	112·7 (3)	C2*B*—C3*B*—C4*B*	112·8 (3)
O3*A*—C3*A*—C4*A*	102·8 (3)	O3*B*—C3*B*—C4*B*	103·7 (3)
C3*A*—C4*A*—O4*A*	103·8 (3)	C3*B*—C4*B*—O4*B*	103·9 (3)
C3*A*—C4*A*—C5*A*	112·1 (3)	C3*B*—C4*B*—C5*B*	113·0 (3)
O4*A*—C4*A*—C5*A*	110·4 (3)	O4*B*—C4*B*—C5*B*	109·8 (3)
C4*A*—C5*A*—O5*A*	107·8 (3)	C4*B*—C5*B*—O5*B*	108·9 (3)
C4*A*—C5*A*—C8*A*	114·4 (3)	C4*B*—C5*B*—C8*B*	113·1 (3)
O5*A*—C5*A*—C8*A*	106·3 (3)	O5*B*—C5*B*—C8*B*	106·2 (3)
C5*A*—O5*A*—C6*A*	111·9 (3)	C5*B*—O5*B*—C6*B*	109·9 (3)
O5*A*—C6*A*—O6*A*	121·3 (3)	O5*B*—C6*B*—O6*B*	120·6 (3)
O5*A*—C6*A*—C7*A*	109·9 (3)	O5*B*—C6*B*—C7*B*	111·0 (3)
O6*A*—C6*A*—C7*A*	128·6 (3)	O6*B*—C6*B*—C7*B*	128·5 (3)
C6*A*—C7*A*—C8*A*	105·2 (3)	C6*B*—C7*B*—C8*B*	105·0 (3)
C1*A*—C8*A*—C5*A*	111·0 (3)	C1*B*—C8*B*—C5*B*	111·7 (3)
C1*A*—C8*A*—C7*A*	116·6 (3)	C1*B*—C8*B*—C7*B*	116·4 (3)
C5*A*—C8*A*—C7*A*	103·9 (3)	C5*B*—C8*B*—C7*B*	102·7 (3)
C1*A*—C11*A*—O1*A*	123·8 (3)	C1*B*—C11*B*—O1*B*	126·0 (3)
C1*A*—C11*A*—O2*A*	112·7 (3)	C1*B*—C11*B*—O2*B*	111·9 (3)
O1*A*—C11*A*—O2*A*	123·4 (3)	O1*B*—C11*B*—O2*B*	122·0 (3)
C11*A*—O2*A*—C12*A*	117·6 (3)	C11*B*—O2*B*—C12*B*	118·0 (3)
C3*A*—O3*A*—C14*A*	107·6 (3)	C3*B*—O3*B*—C14*B*	105·7 (3)
O3*A*—C14*A*—O4*A*	106·4 (4)	O3*B*—C14*B*—O4*B*	103·4 (3)
O3*A*—C14*A*—C15*A*	109·4 (4)	O3*B*—C14*B*—C15*B*	108·5 (4)
O3*A*—C14*A*—C16*A*	110·3 (4)	O3*B*—C14*B*—C16*B*	110·5 (4)
C4*A*—O4*A*—C14*A*	109·6 (3)	C4*B*—O4*B*—C14*B*	108·8 (3)
O4*A*—C14*A*—C15*A*	109·9 (4)	O4*B*—C14*B*—C15*B*	109·4 (4)
O4*A*—C14*A*—C16*A*	106·7 (4)	O4*B*—C14*B*—C16*B*	111·4 (4)
C15*A*—C14*A*—C16*A*	113·9 (5)	C15*B*—C14*B*—C16*B*	113·2 (4)

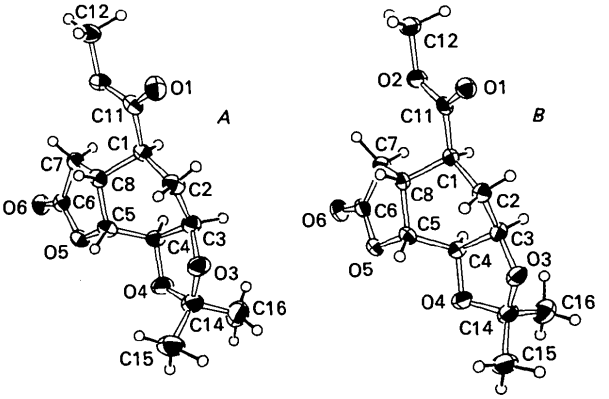

Fig. 1. An *ORTEP* diagram of the title compound with the H atoms and the atomic numbering shown. Ellipsoids represent 30% probability. Represented are molecules *A* and *B*.

Related literature. Intramolecular free-radical mediated cyclization of chloromethyl ester onto an α,β-unsaturated ester has not been considered to be a favored process, see Surzur & Bertrand (1988), Curran (1988) and Giese (1986). The present case represents a preparatively useful method for butyrolactones and it illustrates the feasibility of the reaction.

We thank 'Le Ministère de l'Education du Québec' for financial support and Professor A. L. Beauchamp for assistance in the collection of data and help in resolution of the structure.

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