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1-Carboxy-*trans*-bicyclo[4.4.0]decan-3-one Ethylene Acetal {*trans*-Hexahydrospiro-[1,3-dioxolane-2,2′(1′*H*)-naphthalene]-8′a(3′*H*)-carboxylic Acid}

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Abstract. $C_{13}H_{20}O_4$, $M_r = 240{\cdot}16$, orthorhombic, $Fdd2$, $a = 11{\cdot}913\,(12)$, $b = 37{\cdot}825\,(38)$, $c = 10{\cdot}789\,(11)$ Å, $Z = 16$, $D_x = 1{\cdot}31$ g cm^{-3}. Intermolecular hydrogen bonds between carboxyl groups link pairs of molecules related by the [001] diad axes into dimers.

Introduction. The title compound (m.p. 130·5–131·5 °C) was designed and synthesized (details to be published elsewhere) with the hope that intramolecular hydrogen bonding between the axial carboxyl group and the axial acetal O atom might lead to distortions of the acetal ring, which could possibly throw light on the mechanism of acid-catalysed hydrolysis of cyclic acetals. However, the crystal structure analysis shows that this hope was illusory – the hydrogen bonds formed are intermolecular, between carboxyl groups, rather than intramolecular.

Crystals were obtained by slow evaporation of a solution in ethyl acetate. Intensities from a crystal, about 0·4 mm in edge, were collected on an automated Enraf–Nonius CAD-4 diffractometer with graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0{\cdot}71069$ Å, $\mu = 1{\cdot}04$ cm^{-1}); 1257 reflexions ($2\theta < 52°$) were measured {901 'observed' [$I \geq 3\sigma(I)$]}. The structure (Fig. 1) was solved by direct methods (*MULTAN*, Germain, Main & Woolfson, 1970) and refined by full-matrix least squares (XRAY system, Stewart, Kruger, Ammon, Dickinson & Hall, 1972) with unit weights for observed reflexions. At an intermediate stage, all H atoms were located from a difference map. The final R was 0·067, including extinction corrections. Final positional and mean thermal parameters are given in Table 1,* and bond distances, bond angles and torsion angles in Fig. 2.

Table 1. *Atomic coordinates and isotropic U values* (× 10^4 *for* C *and* O, × 10^3 *for* H *atoms; e.s.d.'s in parentheses*)

Non-hydrogen atoms were refined anisotropically.

	x	y	z	$\bar{U}$ (Å^2)		x	y	z	U (Å^2)
C(1′)	3116 (5)	9061 (2)	4061 (7)	373 (37)	H(1)C(1′)	368 (6)	897 (2)	415 (7)	54 (21)
C(2′)	2568 (6)	9209 (2)	2915 (6)	358 (36)	H(2)C(1′)	274 (5)	886 (2)	437 (6)	29 (16)
C(3′)	1403 (6)	9356 (2)	3155 (7)	425 (39)	H(1)C(3′)	123 (6)	954 (2)	223 (9)	83 (28)
C(4′)	1412 (5)	9612 (2)	4262 (6)	347 (35)	H(2)C(3′)	96 (6)	918 (2)	333 (7)	56 (23)
C(5′)	1780 (5)	9638 (2)	6623 (7)	427 (39)	H(1)C(4′)	178 (5)	985 (2)	393 (6)	28 (17)
C(6′)	2241 (6)	9443 (2)	7731 (7)	478 (43)	H(2)C(4′)	53 (5)	971 (2)	429 (6)	33 (17)
C(7′)	3447 (6)	9324 (2)	7527 (7)	486 (42)	H(1)C(5′)	212 (6)	989 (2)	643 (7)	46 (20)
C(8′)	3537 (5)	9109 (2)	6343 (6)	362 (34)	H(2)C(5′)	113 (7)	973 (2)	680 (9)	72 (31)
C(9′)	3120 (5)	9314 (2)	5181 (6)	279 (32)	H(1)C(6′)	219 (6)	962 (2)	849 (6)	49 (20)
C(10′)	1893 (4)	9436 (2)	5429 (6)	281 (30)	H(2)C(6′)	175 (4)	925 (1)	777 (5)	25 (15)
C(11′)	3913 (4)	9614 (2)	4948 (7)	308 (31)	H(1)C(7′)	378 (7)	956 (3)	768 (10)	106 (34)
O(12′)	3666 (3)	9925 (1)	4982 (6)	436 (26)	H(2)C(7′)	371 (5)	918 (2)	830 (6)	37 (19)
O(13′)	4965 (3)	9514 (1)	4787 (6)	488 (28)	H(1)C(8′)	421 (5)	901 (2)	638 (6)	44 (19)
O(1)	2513 (4)	8936 (1)	2016 (5)	492 (28)	H(2)C(8′)	312 (5)	892 (2)	667 (6)	35 (18)
O(3)	3252 (4)	9479 (1)	2386 (5)	479 (28)	HC(10′)	149 (4)	918 (1)	546 (5)	13 (13)
C(4)	3497 (8)	9384 (2)	1170 (9)	658 (57)	H(1)C(4)	348 (9)	966 (3)	82 (11)	125 (40)
C(5)	2723 (7)	9098 (2)	841 (7)	551 (50)	H(2)C(4)	421 (8)	929 (2)	159 (10)	123 (37)
					H(1)C(5)	218 (6)	922 (2)	49 (7)	57 (23)
					H(2)C(5)	295 (7)	883 (2)	23 (9)	79 (28)
					HO(13′)	546 (7)	974 (2)	440 (8)	84 (30)

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* Lists of structure factors and anisotropic thermal parameters (for C and O atoms) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33124 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

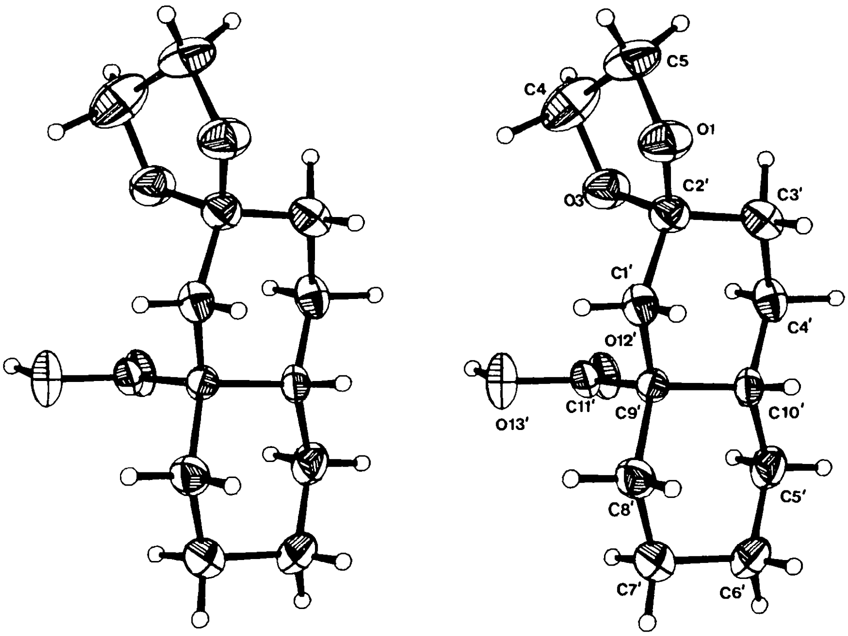
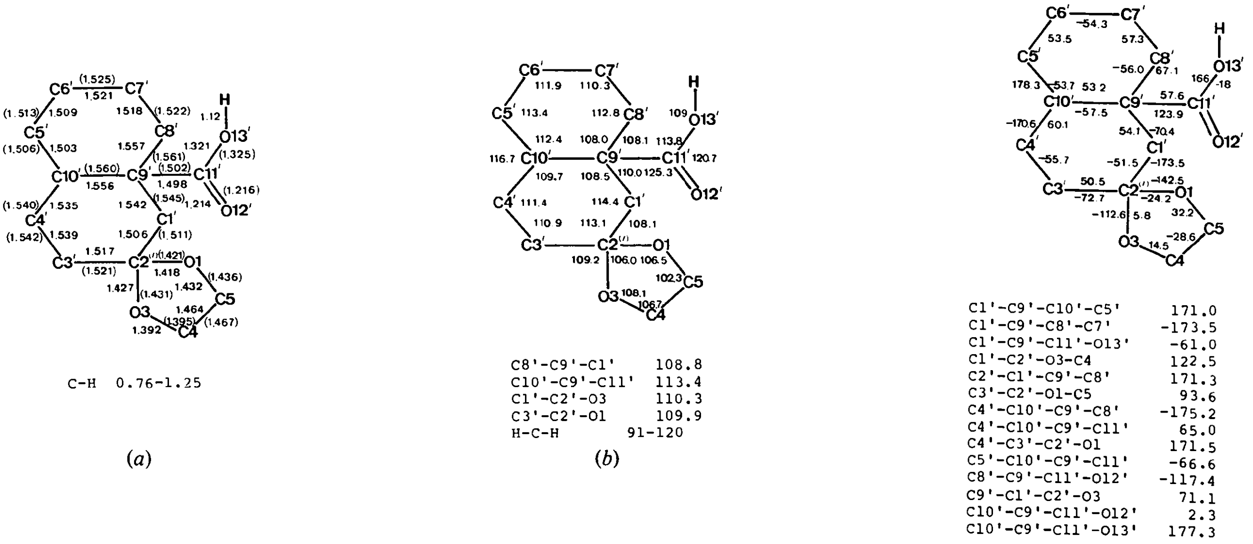


Fig. 1. Stereoscopic view of the molecule drawn by *ORTEP* (Johnson, 1965). The thermal-vibration ellipsoids are at the 50% probability level.



C-H 0.76-1.25

(*a*)

C8'-C9'-C1'	108.8
C10'-C9'-C11'	113.4
C1'-C2'-O3	110.3
C3'-C2'-O1	109.9
H-C-H	91-120

(*b*)

C1'-C9'-C10'-C5'	171.0
C1'-C9'-C8'-C7'	-173.5
C1'-C9'-C11'-O13'	-61.0
C1'-C2'-O3-C4	122.5
C2'-C1'-C9'-C8'	171.3
C3'-C2'-O1-C5	93.6
C4'-C10'-C9'-C8'	-175.2
C4'-C10'-C9'-C11'	65.0
C4'-C3'-C2'-O1	171.5
C5'-C10'-C9'-C11'	-66.6
C8'-C9'-C11'-O12'	-117.4
C9'-C1'-C2'-O3	71.1
C10'-C9'-C11'-O12'	2.3
C10'-C9'-C11'-O13'	177.3

(*c*)

Fig. 2. (*a*) Bond lengths (Å) (values corrected for molecular libration in brackets), (*b*) bond angles (°) and (*c*) torsion angles (°). E.s.d.'s are 0·007–0·012 Å for bond lengths, 0·5–0·7° for bond angles not involving H atoms and somewhat larger for torsion angles.

Discussion. As seen from Fig. 1, the mean plane of the carboxyl group is virtually coplanar with the central C(9')–C(10') bond of the decalin system, and hence the intramolecular hydrogen bonding we had hoped to find between this group and the axial oxygen O(3) of the acetal ring is absent. Instead, pairs of molecules related by a diad axis are linked (Fig. 3) by intermolecular hydrogen bonds (O···O, 2·68 Å) to form the cyclic dimers characteristic of monocarboxylic acids in the crystalline state (Leiserowitz, 1976). However, since O(3) and the carboxyl C(11') are in 1,3-diaxial relationship, they can hardly avoid some interaction with each other; the O···C distance is 2·92 Å, and C(11') is displaced by 0·033 (9) Å from the plane of its three bonded neighbours *towards* O(3), indicative of an attraction between the two atoms

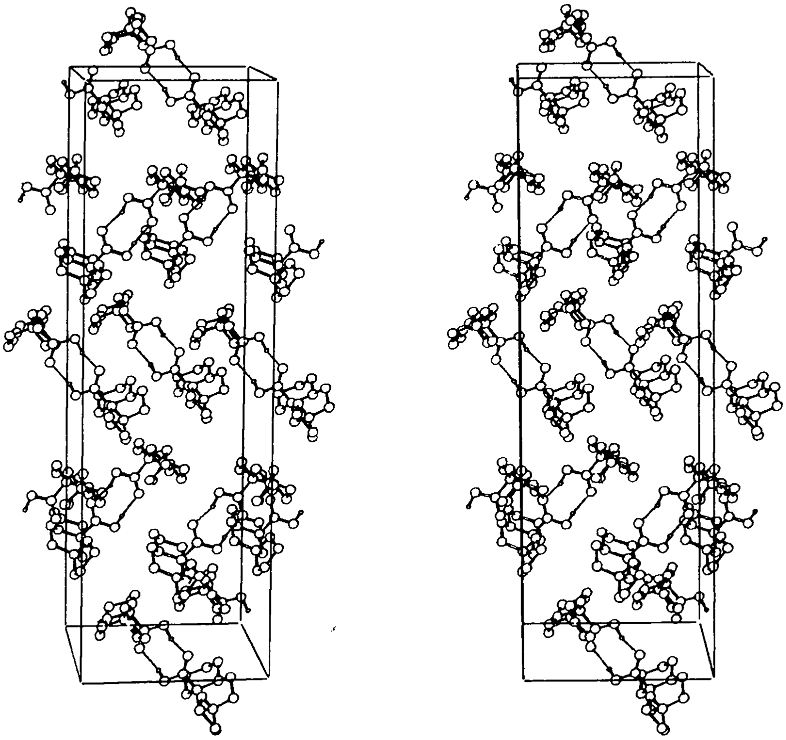


Fig. 3. Stereoscopic view of the crystal structure drawn by *ORTEP* (Johnson, 1965). The axial directions are **a**→, **b**↑, and **c** into the plane of the paper. Hydrogen bonds are indicated.

concerned. We interpret this as evidence of incipient nucleophilic attack of the acetal O on the carboxyl C; many other analogous examples are known (Bürgi, Shefter & Dunitz, 1974; Kaftory & Dunitz, 1975, 1976; Schweizer, 1977).

Bond lengths and angles in the acetal ring resemble those in 1,4,9,12-tetraoxadispiro[4.2.4.2]tetradecane (Chadwick, Dunitz & Schweizer, 1977), except that the axial bond C(2)–O(3) is now marginally longer (~0·01 Å) than the equatorial bond C(2)–O(1) and the O(3)–C(4) bond is now somewhat shortened. It may seem rather tempting to couple these changes with the O(3)···C(11′) interaction and interpret them in terms of an incipient ring-opening process, but it must be admitted that they are of dubious significance, mainly because of the difficulty of making adequate corrections for the large, anisotropic thermal motion of the atoms of the acetal ring (see Fig. 1). For example, the apparent shortening of the C(4)–C(5) bond is almost certainly due to inadequacy of the thermal corrections applied.

In this connexion, it should be mentioned that analysis of the vibrational ellipsoids in terms of rigid-body motion (Schomaker & Trueblood, 1968) leads to unsatisfactory agreement between observed and calculated tensor components [$\langle \Delta^2(U_{ij})\rangle^{1/2}$ = 0·0064 Å^2, $\langle \sigma^2(U_{ij})\rangle^{1/2}$ = 0·0034 Å^2]. The largest discrepancies occur for the two C atoms of the acetal ring, and the shapes of the vibrational ellipsoids suggest that this ring may be undergoing a considerable puckering motion, similar to that inferred for the dispiro compound. As in the dispiro molecule, the conformation of the acetal ring is nearer to a twist than to an envelope, but the approximate twofold axis now passes through the axial O(3) rather than through the equatorial O(1). If the roles of these two atoms are interchanged, the acetal-ring torsion angles are almost identical in the two molecules.

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3-Amino-3-hydroxy-*trans*-bicyclo[4.4.0]decane-1-carboxylic Acid Lactam (*trans*-8a,2-Decahydro-2-naphtholcarbolactam)

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Abstract. $C_{11}H_{17}NO_2$, M_r = 195·14, monoclinic, $C2/c$, a = 28·159 (28), b = 7·404 (7), c = 10·635 (11) Å, β = 70·35 (2)°, Z = 8, D_x = 1·24 g cm^{-3}. The title compound is usually named as the corresponding carboxamide–ketone isomer [octahydro-3-oxo-4a(2*H*)-naphthalenecarboxamide] but it exists both in the crystalline state and in solution as the lactam–alcohol. An appreciable out-of-plane distortion of the amide group can be detected. The hydroxyl and amide H atoms both participate in intermolecular hydrogen bonds.

Introduction. The compound (m.p. 165·5–166 °C) was synthesized by the method of Meyer & Schnautz (1962). Crystals were obtained by slow cooling of a saturated solution (1:1 ethyl acetate–cyclohexane). Data collection, structure analysis and refinement followed much the same lines as in Chadwick & Dunitz (1978); the crystal used was 0·3 × 0·3 × 0·2 mm on edge, and 2276 reflexions ($2\theta < 54°$) were measured, 1787 with $I \geq 3\sigma(I)$. The final R was 0·040 (no extinction correction required). Final positional and mean thermal parameters are given in Table 1.* Fig. 1 shows the molecular structure, Fig. 2 bond lengths,

Table 1. *Atomic coordinates and isotropic U values* (× 10^4 *for* C *and* O, × 10^3 *for* H *atoms; e.s.d.'s in parentheses*)

Non-hydrogen atoms were refined anisotropically.

	x	y	z	$\bar{U}$ (Å^2)		x	y	z	U (Å^2)
C(1)	9391 (1)	5532 (4)	934 (3)	469 (17)	H(1)C(1)	956 (1)	549 (3)	−11 (3)	39 (7)
C(2)	9581 (1)	7209 (5)	1472 (3)	486 (18)	H(2)C(1)	953 (1)	441 (4)	118 (3)	67 (10)
C(3)	9314 (1)	8898 (4)	1257 (3)	371 (14)	H(1)C(2)	996 (1)	730 (4)	102 (2)	49 (8)
C(4)	8750 (1)	8712 (4)	1965 (3)	400 (15)	H(2)C(2)	954 (1)	712 (4)	243 (3)	58 (8)
C(5)	8047 (1)	7276 (5)	1262 (3)	547 (19)	H(1)C(4)	856 (1)	991 (4)	197 (3)	49 (8)
C(6)	7897 (1)	5729 (6)	523 (4)	675 (24)	H(2)C(4)	866 (1)	830 (4)	292 (3)	45 (8)
C(7)	8101 (1)	3930 (5)	783 (4)	625 (22)	H(1)C(5)	794 (1)	841 (5)	98 (4)	88 (11)
C(8)	8668 (1)	4017 (4)	462 (3)	488 (18)	H(2)C(5)	788 (1)	710 (4)	225 (3)	53 (8)
C(9)	8819 (1)	5488 (4)	1257 (3)	368 (14)	H(1)C(6)	801 (1)	602 (4)	−43 (3)	76 (9)
C(10)	8611 (1)	7366 (4)	1050 (3)	343 (13)	H(2)C(6)	753 (2)	575 (6)	69 (4)	98 (13)
C(11)	8944 (1)	8055 (4)	−317 (3)	387 (14)	H(1)C(7)	800 (1)	295 (5)	27 (4)	79 (11)
O(1)	8884 (1)	7771 (3)	−1394 (2)	557 (13)	H(2)C(7)	794 (1)	366 (5)	174 (3)	67 (10)
O(2)	9547 (1)	10437 (3)	1571 (2)	548 (13)	H(1)C(8)	882 (1)	429 (4)	−51 (3)	53 (8)
N	9326 (1)	8988 (3)	−136 (2)	387 (12)	H(2)C(8)	883 (1)	280 (5)	57 (3)	73 (10)
					HC(9)	864 (1)	528 (3)	224 (3)	38 (7)
					HN	963 (1)	925 (4)	−81 (3)	62 (8)
					HO(2)	928 (1)	1104 (5)	223 (4)	102 (11)

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