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*Acta Cryst.* (1995). **C51**, 1204–1207

## An Unusual C6-Spiro-Fused Cyclouridine Derivative

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(Received 27 September 1994; accepted 3 November 1994)

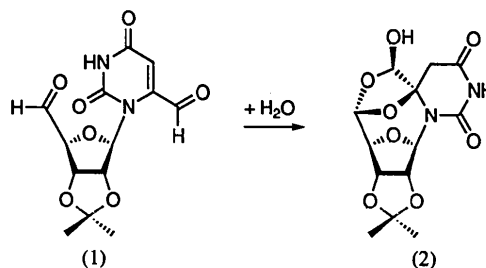
### Abstract

The title compound, [3*S*,4*S*,5*R*-(1*β*,3*β*,4*αα*,7*αα*,13*αβ*)]-1,4,4*a*,7*a*,8,13*a*-hexahydro-1-hydroxy-6,6-dimethyl-3,13*a*:4,8-diepoxy-3*H*,6*H*-dioxolano[4,5-*f*]pyrimido[6,1-*c*][1,4]oxazine-10,12(11*H*,13*H*)-dione, C<sub>13</sub>H<sub>16</sub>N<sub>2</sub>O<sub>8</sub>, is a structurally unusual C6-spiro-fused *anti*-locked dihydrouridine nucleoside derivative arising from the monohydration and subsequent two-step cyclization of a uridine-6,5'-dicarboxaldehyde. The torsion angle O4'—C1'—N1—C6 of the glycosidic linkage is 42.7 (4)°.

### Comment

Uridine-6-carboxaldehyde was prepared recently and shown to exhibit a strong tendency towards undergoing hydration and 7,5'-cyclic hemiacetal formation in solution (Groziak & Koohang, 1992). The findings of a detailed investigation (Groziak, Koohang, Stevens & Robinson, 1993) of this ribonucleoside and its 2'-deoxyribofuranose and arabinofuranose counterparts have encouraged us to undertake the

development of several new classes of uridine-based cyclonucleosides based upon the 6-formyluridine framework. Among these is a new class of cyclonucleosides expected to arise from hydration reactions involving both formyl groups present in certain uridine-6,5'-dicarboxaldehydes. In the first example of such a cyclonucleoside-forming hydration process, we report that 2',3'-*O*-isopropylideneuridine-6,5'-dicarboxaldehyde, (1), hydrates in, and crystallizes out of, aqueous solution as the title compound (2). The enantiomorphic identity of (2) was established through its method of synthesis, which did not alter that of the commercially available starting material uridine, known to possess a  $\beta$ -glycosidic linkage and a ribofuranosyl moiety of the *D* configuration.



An *ORTEP* (Johnson, 1965) view of (2), together with the standard uridine atom numbering, is provided in Fig. 1. The molecular structure of (2) is a unique blend of some of the structural features determined for certain 6,5'-methano-bridged uridines (Yamagata, Tomita, Usui, Sano & Ueda, 1989), for a 2,5':2,6'-dianhydro derivative of a 4-*N*-acetylcytosine talofuranoside (David, de Sennyey, Pascard & Guilhem, 1981) and for a 6,3':6,5'-dianhydro derivative of a 5,5-dibromo-5,6-dihydro-6,6-dihydroxyuracil xylofuranoside (Honjo, Maruyama, Wada & Kamiya, 1984). It is useful to view the cyclonucleoside (2), formally the (6*R*,7*R*,5'*S*)-6,5':7,5'-dianhydro version of 5,6-dihydro-6,5'-dihydroxy-6-(dihydroxymethyl)-1-(2,3-*O*-isopropylidene- $\beta$ -*D*-ribofuranosyl)uracil, as simply a monohydrate of (1) arising from a three-step kinetic sequence that involves initially a hydration of the C6-formyl substituent, followed by a 1,2-addition of a hydroxyl group of the resultant 6-hydrate moiety onto the ribofuranose 5'-carboxaldehyde, and finally a Michael-type addition of the hydroxyl group of the resultant 5'-hemiacetal moiety onto the C6 position of the uracil ring. The 7*R* stereochemical configuration in (2) is identical to that found in the 7,5'-cyclic hemiacetal structure of uridine-6-carboxaldehyde (Groziak, Koohang, Stevens & Robinson, 1993), while the 5'*S* and 6*R* configurations can be viewed as the outcomes of stereofacially specific hydroxyl-group addition reactions to the *si* face of the 5'-carbonyl C atom and to the *re* face of the C6 trigonal C atom, respectively. The stereofacial intramolecular 1,2-addition to a nucleoside 5'-carboxaldehyde producing 5'*S* stereochemistry is well precedented (Rabi & Fox, 1972).

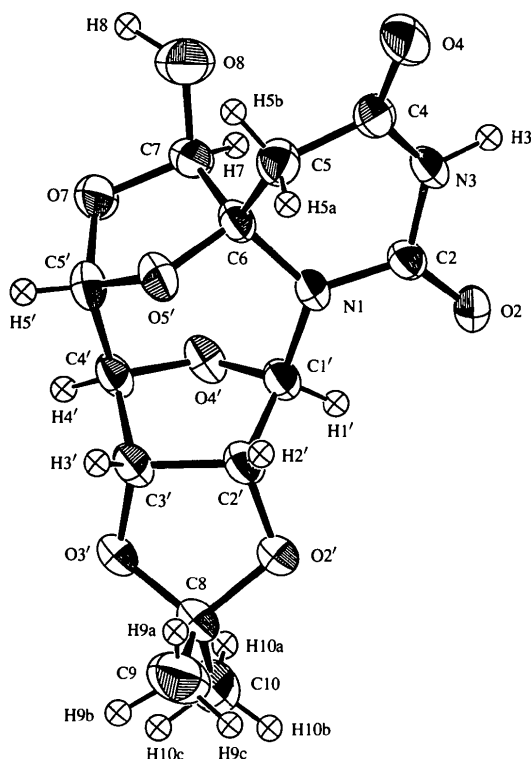


Fig. 1. Molecular configuration and atom-numbering scheme for compound (2) with displacement ellipsoids at the 50% probability level. H atoms are shown as isotropic spheres of arbitrary radii.

The dihydrouracil ring of (2) is puckered such that C5 and C6 reside on opposite sides of a nearly coplanar (0.05 Å r.m.s deviation) N1, C2, N3 and C4 atom set, similar to that found for 1-methyl-5-fluoro-6-methoxy-5,6-dihydrouracil (James & Matsushima, 1976), 1-(*N*-methylcarbamoyl)-3-methyl-5,6-dihydrouracil (Parthasarathy, Ohrt, Dutta & Chheda, 1973), the twist half-chair structure of 5,6-dihydrouracil itself (Rohrer & Sundaralingam, 1970) and in particular the 'B' molecule of crystalline 5,6-dihydrouridine (Suck, Saenger & Zechmeister, 1972). The diastereotopic H5*a* and H5*b* atoms occupy pseudo-axial and pseudo-equatorial positions, respectively, on the dihydrouracil ring and the torsion angle H5*a*—C5—C4—O4 of 87° suggests that atom H5*a* should be the more acidic of the two. This nearly optimal orientation at the C atom  $\alpha$  to the C4=O4 carbonyl group, together with any steric hindrance afforded H5*b* by the nearby (2.307 Å) O8 atom, provides an explanation for our observation that only atom H5*a* exchanges rapidly in neutral D<sub>2</sub>O solution at room temperature. The furanose ring of (2) is puckered with an O4'-*exo* conformation, a feature common to many 2',3'-*O*-isopropylidenedated ribonucleosides. The torsion angle O4'—C1'—N1—C6 of 42.7 (4)°, this pyrimidine nucleoside's glycosidic torsion angle  $\chi_{CN}$ , is indicative of an *anti*-locked conformation.

A view of the unit cell with the hydrogen-bonding scheme for (2) is shown in Fig. 2. The intermolecular hydrogen-bond network consists of O8—H8···O2(1 + *x*, *y*, *z*) and N3—H3···O3'(1 + *x*, *y*, 1 + *z*) interactions (see Table 2). These two associations delineate planar sheets of hydrogen-bond-associated molecules, with neighboring sheets oriented in an antiparallel fashion.

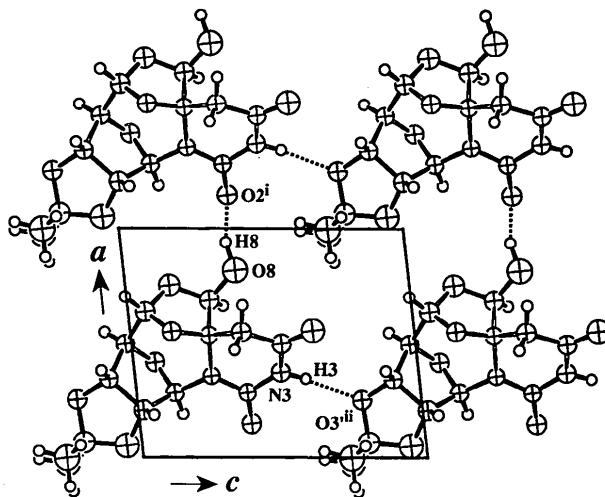


Fig. 2. Molecular packing and hydrogen bonding of (2) as viewed down the *b* axis. Note that the four molecules shown are identical in orientation and are related to each other by simple *a* and *c* axial translations. The hydrogen bonding, shown by dashed lines, is confined to the *ac* plane forming a sheet normal to [010]. The twofold screw axis and unit translations along *b* will repeat the sheet infinitely.

## Experimental

The precursor compound (1) was prepared from uridine according to a multistep synthesis (Lin & Groziak, unpublished). X-ray quality single crystals of the title compound were obtained *via* slow evaporation of an aqueous solution of (1) in an NaOH-containing desiccator charged with an argon atmosphere. Crystals of (2) thus obtained had m.p. 478–483 K (decomposition) and showed <sup>1</sup>H, <sup>13</sup>C, COSY and HETCOR NMR, and low- and high-resolution MS characteristics consistent with the solid-state structure reported herein.

### Crystal data

C<sub>13</sub>H<sub>16</sub>N<sub>2</sub>O<sub>8</sub>  
*M<sub>r</sub>* = 328.28  
 Monoclinic  
*P*2<sub>1</sub>  
*a* = 7.569 (1) Å  
*b* = 9.738 (2) Å  
*c* = 9.503 (1) Å  
 $\beta$  = 96.32 (1)°  
*V* = 696.2 (3) Å<sup>3</sup>  
*Z* = 2  
*D<sub>x</sub>* = 1.566 Mg m<sup>-3</sup>

Mo *K*α radiation  
 $\lambda$  = 0.71069 Å  
 Cell parameters from 25 reflections  
 $\theta$  = 18.55–19.92°  
 $\mu$  = 0.123 mm<sup>-1</sup>  
*T* = 296 K  
 Prism  
 0.38 × 0.33 × 0.20 mm  
 Pale yellow

## Data collection

Rigaku AFC-5S diffractometer	$R_{\text{int}} = 0.016$
$\omega/2\theta$ scans ( $2^\circ \text{ min}^{-1}$ in $\omega$ )	$\theta_{\text{max}} = 25^\circ$
Absorption correction: none	$h = 0 \rightarrow 8$
1405 measured reflections	$k = 0 \rightarrow 11$
1302 independent reflections	$l = -11 \rightarrow 11$
1238 observed reflections [ $I > \sigma(I)$ ]	3 standard reflections monitored every 100 reflections intensity decay: 0.6%

## Refinement

Refinement on $F$	$w = 4F_o^2/\sigma^2(F_o^2)$
$R = 0.035$	$(\Delta/\sigma)_{\text{max}} = 0.0001$
$wR = 0.043$	$\Delta\rho_{\text{max}} = 0.26 \text{ e } \text{\AA}^{-3}$
$S = 1.96$	$\Delta\rho_{\text{min}} = -0.19 \text{ e } \text{\AA}^{-3}$
1238 reflections	Atomic scattering factors from <i>International Tables for X-ray Crystallography</i> (1974, Vol. IV, Table 2.3.1)
207 parameters	
H atoms calculated (C—H, N—H 0.95 Å), except for H7 and H8 which were obtained from a difference map	

C7—O7—C5'	109.3 (2)	O7—C7—C6	104.5 (2)
C8—O2'—C2'	108.5 (2)	O8—C7—C6	109.2 (3)
C8—O3'—C3'	107.2 (2)	O2'—C8—O3'	103.8 (2)
C1'—O4'—C4'	108.3 (2)	O1'—C8—C9	111.6 (3)
C6—O5'—C5'	107.2 (2)	O2'—C8—C10	108.5 (3)
C2—N1—C6	121.0 (2)	O3'—C8—C9	110.5 (3)
C2—N1—C1'	118.3 (2)	O3'—C8—C10	107.7 (3)
C6—N1—C1'	118.5 (2)	C9—C8—C10	114.2 (3)
C2—N3—C4	126.4 (3)	O4'—C1'—N1	110.8 (2)
O2—C2—N1	124.4 (3)	O4'—C1'—C2'	104.4 (2)
O2—C2—N3	119.5 (2)	N1—C1'—C2'	114.9 (3)
N1—C2—N3	116.1 (3)	O2'—C2'—C1'	107.7 (3)
O4—C4—N3	121.6 (3)	O2'—C2'—C3'	104.3 (2)
O4—C4—C5	123.9 (3)	C1'—C2'—C3'	105.2 (2)
N3—C4—C5	114.5 (3)	O3'—C3'—C2'	104.1 (2)
C4—C5—C6	112.3 (3)	O3'—C3'—C4'	110.5 (3)
O5'—C6—N1	109.2 (2)	C2'—C3'—C4'	103.7 (2)
O5'—C6—C5	108.2 (3)	O4'—C4'—C3'	105.0 (3)
O5'—C6—C7	103.7 (2)	O4'—C4'—C5'	109.4 (2)
N1—C6—C5	109.0 (2)	C3'—C4'—C5'	111.4 (3)
N1—C6—C7	112.1 (3)	O7—C5'—O5'	105.6 (2)
C5—C6—C7	114.4 (3)	O7—C5'—C4'	112.2 (3)
O7—C7—O8	110.2 (3)	O5'—C5'—C4'	108.5 (3)

D—H...A	D—H	H...A	D...A	D—H...A
O8—H8...O2'	1.09	1.66	2.711 (4)	160
N3—H3...O3' <sup>ii</sup>	0.95	2.03	2.930 (3)	158

Symmetry codes: (i)  $1 + x, y, z$ ; (ii)  $x, y, 1 + z$ .

Weak reflections [ $I < 10\sigma(I)$ ] were rescanned (maximum of 3 rescans) and the counts accumulated to improve accuracy.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN LS*. Molecular graphics: *TEXSAN*, *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *TEXSAN FINISH*.

This work was supported by a grant from the Office of Research Development and Administration of Southern Illinois University at Carbondale.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1041). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

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

	x	y	z	$U_{\text{eq}}$
O2	0.1479 (3)	0.3471	0.3925 (2)	0.042 (1)
O4	0.5519 (4)	0.6156 (4)	0.6423 (3)	0.062 (1)
O7	0.7494 (3)	0.4079 (4)	0.1546 (2)	0.051 (1)
O8	0.8158 (3)	0.4517 (5)	0.3907 (3)	0.071 (1)
O2'	0.0507 (3)	0.4198 (5)	-0.0531 (2)	0.064 (1)
O3'	0.2511 (3)	0.4079 (4)	-0.2090 (2)	0.040 (1)
O4'	0.4141 (3)	0.3065 (4)	0.0764 (2)	0.038 (1)
O5'	0.5477 (3)	0.5791 (4)	0.1454 (2)	0.038 (1)
N1	0.3550 (3)	0.4483 (4)	0.2687 (2)	0.031 (1)
N3	0.3714 (3)	0.4661 (4)	0.5144 (2)	0.039 (1)
C2	0.2824 (4)	0.4164 (4)	0.3888 (3)	0.032 (1)
C4	0.4949 (4)	0.5694 (5)	0.5273 (3)	0.039 (1)
C5	0.5449 (5)	0.6234 (5)	0.3892 (4)	0.042 (1)
C6	0.5312 (4)	0.5147 (4)	0.2748 (3)	0.033 (1)
C7	0.6853 (4)	0.4080 (5)	0.2891 (3)	0.042 (1)
C8	0.0647 (4)	0.4218 (6)	-0.2002 (3)	0.049 (1)
C9	-0.0029 (6)	0.5546 (7)	-0.2667 (5)	0.072 (2)
C10	-0.0259 (6)	0.2950 (6)	-0.2660 (4)	0.072 (2)
C1'	0.2820 (4)	0.3819 (5)	0.1354 (3)	0.035 (1)
C2'	0.2063 (4)	0.4811 (5)	0.0185 (3)	0.041 (1)
C3'	0.3408 (4)	0.4793 (4)	-0.0911 (3)	0.036 (1)
C4'	0.4930 (4)	0.3938 (5)	-0.0210 (3)	0.035 (1)
C5'	0.6343 (4)	0.4834 (5)	0.0600 (3)	0.041 (1)

Table 2. Bond lengths ( $\text{\AA}$ ), angles ( $^\circ$ ) and hydrogen-bonding geometry ( $\text{\AA}, ^\circ$ )

O2—C2	1.225 (4)	N1—C6	1.478 (4)
O4—C4	1.216 (4)	N1—C1'	1.474 (4)
O7—C7	1.416 (4)	N3—C2	1.392 (4)
O7—C5'	1.391 (4)	N3—C4	1.370 (5)
O8—C7	1.370 (4)	C4—C5	1.501 (5)
O2'—C8	1.414 (4)	C5—C6	1.513 (4)
O2'—C2'	1.424 (4)	C6—C7	1.557 (5)
O3'—C8	1.429 (4)	C8—C9	1.504 (7)
O3'—C3'	1.426 (4)	C8—C10	1.514 (6)
O4'—C1'	1.406 (4)	C1'—C2'	1.536 (5)
O4'—C4'	1.434 (4)	C2'—C3'	1.535 (4)
O5'—C6	1.399 (4)	C3'—C4'	1.515 (5)
O5'—C5'	1.440 (4)	C4'—C5'	1.523 (5)
N1—C2	1.356 (4)		

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*Acta Cryst.* (1995). **C51**, 1207–1209

### Tris(*O*-4-*tert*-butylphenyl)thiophosphate, C<sub>30</sub>H<sub>39</sub>O<sub>3</sub>PS

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(Received 19 September 1994; accepted 24 November 1994)

#### Abstract

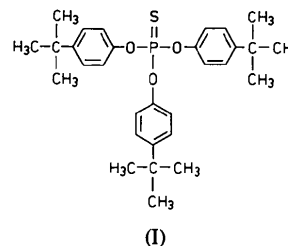
The P—O bond of the title compound is aligned along a threefold symmetry axis, making the three 4-(*tert*-butyl)phenyl groups crystallographically equivalent. The P atom is bonded to three O and one S atom, forming a distorted tetrahedron: O—P—S = 117(1), O—P—O = 100(1)°, P—S = 1.908(1), P—O = 1.579(2) Å. Neither the phenyl ring nor the attached *tert*-butyl group exhibit any unexpected geometrical features.

#### Comment

Some sulfur-containing organo-phosphorus compounds have received attention because of their insecticide activity (*e.g.* Schrader, 1954, 1961; Duspiva, 1954; Engelhard, Prehal & Menner, 1967). Therefore, we have synthesized a number of such compounds and investigated their chemical, thermal and spectroscopic properties (Odabaşoğlu & Gümrükçüoğlu, 1993).

The asymmetric unit of the title compound, (I), comprises one third of the formula unit; P and S are located in special positions on the threefold axis. Judged from the displacement parameters, there is no indication

of any disorder in the crystal structure; the displacement ellipsoids suggest torsional oscillation of the *tert*-butyl groups.



The geometry about the P atom corresponds to a distorted tetrahedron: the P atom is displaced from the basal plane through the crystallographically equivalent O atoms O(1), O(1<sup>i</sup>) and O(1<sup>ii</sup>) towards the apical atom S(1) by 0.726(2) Å [symmetry codes: (i)  $-x + y, -x, z$ ; (ii)  $-y, x - y, z$ ]. The O—P—S angle [117.4(1)°] is wider and the O—P—O angle [100.5(1)°] is smaller than the ideal tetrahedral angle of 109.5°.

The P=S double-bond distance [1.908(1) Å] is in the range of bond lengths reported by Schomaker & Stevenson (1941) for PSF<sub>3</sub> (1.85 Å) and for PSCl<sub>3</sub> (1.91 Å). Obviously, the electron affinities (2.8, 3.5 and 4.0 for Cl, O and F, respectively) have a distinct effect on the apical P—S bonds: the larger the electron affinity, the shorter the P—S bond. The P—O bond length [1.579(2) Å] agrees with that of the P—OH bond of orthophosphoric acid (1.576 Å; *International Tables for X-ray Crystallography*, 1983, Vol. III).

As a result of the influence of the aromatic ring, the C(4)—O(1) single bond [1.401(3) Å] is slightly

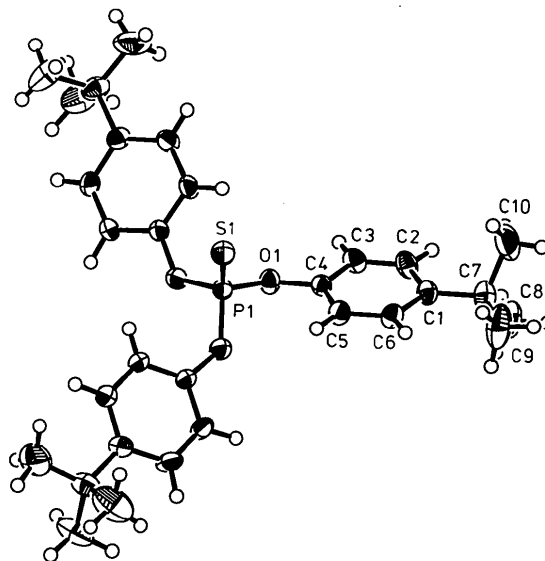


Fig. 1. Perspective view of the molecule, showing 50% probability ellipsoids. The asymmetric unit comprises one third of the molecule.