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The Crystal Structure of Dextrorotatory 2'-O-Tetrahydropyranyluridine

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The dextrorotatory diastereoisomer of 2'-O-tetrahydropyranyluridine ($C_{14}H_{20}N_2O_7$) crystallizes in the orthorhombic space group $P2_12_12_1$ (D_2^4) with $a = 6·716$ (2), $b = 10·124$ (4), $c = 22·720$ (12) Å, and $Z = 4$. The structure has been determined by direct methods and refined to $R = 0·039$ with 1172 reflexions measured on a single-crystal X-ray diffractometer. The absolute configuration about the acetal carbon centre [C(2″)] is R. Conformation of the ribose ring is C(2')-endo. Bond lengths and angles (standard errors 0·004 Å and 0·3° respectively) are similar to those in related compounds. An explanation of the difference in polarity between the two diastereoisomers is given in terms of intramolecular hydrogen bonding in organic solvents.

Introduction

The formation of a chiral acetal carbon atom [C(2″)] during the condensation of dihydropyran with a 2'-hydroxyl group of a nucleoside results in the existence of diastereoisomeric pairs for each 2'-O-tetrahydropyranylnucleoside (e.g., (I) and (II) in Fig. 1) (Griffin, Jarman & Reese, 1968). The physical properties of the diastereoisomers are quite different, allowing convenient separation by fractional crystallization. The more dextrorotatory isomers of (I) and (II) are markedly less polar, possess lower melting points, and are more mobile in chromatographic systems with organic solvents.

An X-ray crystal structure determination of the more laevorotatory isomer of 2'-O-tetrahydropyranyladenosine [ThPA(−)] (II in Fig. 1) (Kennard, Motherwell, Coppola, Griffin, Reese & Larson, 1971) has shown that the acetal carbon atom C(2″) possesses the S absolute configuration in agreement with conclusions reached from studies on the tetrahydropyranyl ethers of a series of six related steroids (Klyne, Mose, Scopes, Holder & Whalley, 1971). In this paper we show that in the more dextrorotatory isomer of 2'-O-tetrahydropyranyluridine [ThPU(+)] (I in Fig. 1) the C(2″) carbon atom has the R absolute configuration.

Experimental method

Dextrorotatory 2'-O-tetrahydropyranyluridine [ThPU(+)] was prepared by the method of Griffin et al. (1968). Crystals suitable for X-ray work were grown from a methylene chloride solution. The space group was assigned unambiguously as $P2_12_12_1$ on the basis of the Laue symmetry and the systematic absences (for $h00$: $h = 2n + 1$; for $0k0$: $k = 2n + 1$; for $00l$: $l = 2n + 1$). The intensities of 2007 reflexions in the hkl and $hk\bar{l}$ quadrants were measured on a Syntex diffractometer from a crystal $0·51 \times 0·39 \times 0·18$ mm with crystal monochromated Mo $K\alpha$ radiation. They were averaged

to give 1197 non-equivalent reflexions of which 25 had intensities less than zero after subtraction of background. The lattice parameters were determined by least-squares calculations from the 2θ values of 13 reflexions [λ(Mo $K\alpha$)=0·71069 Å]. Corrections were made for Lorentz and polarization factors, but not for absorption (maximum error in F resulting from neglect of absorption is 3·5%).

The structure was solved by direct methods (Karle & Karle, 1966) with the programs *SINGEN* and *TANGEN* of the XRAY 71 system (Stewart, Kruger, Kundell & Baldwin, 1971). One enantiomorph-defining and three origin-defining reflexions were used with the $\sum_2$ relations for 152 reflexions with $|E| \geq 1·5$ to calculate several other phases with high probability (Table 1). These, together with one symbolic phase, were used to calculate phases for all 152 reflexions with the unweighted tangent formula. From an E map computed from one of the two resultant sets of phases, enough of the structure could be recognized to allow location of all non-hydrogen atoms. After partial refinement, all the hydrogen atoms could be located from difference maps. A block diagonal least-squares program (*CRYLSQ*) was used to refine all the parameters including the hydrogen temperature factors but excluding the hydrogen positional coordinates. The hydrogen temperature factors were subsequently kept fixed, although those that were implausibly high were reset to more reasonable values. All the remaining parameters were then varied in several more cycles of block-diagonal least-squares calculations. In the final cycle of least-squares refinement the 1172 reflexions with non-

zero intensities were weighted by $w = (\sigma_c^2 + 5 \times 10^{-4}F_o^2)^{-1}$ where σ_c is the standard error attributable to counting statistics. The positional and anisotropic thermal parameters of all non-hydrogen atoms, and the positional parameters of H(13), H(15), H(16), H(O3'), and H(O5') were varied with a full matrix least-squares program (*CUDLS*) written by J. S. Stephens. The final weighted agreement index ($R_2 = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$) was 0·041 and the unweighted agreement index ($R_1 = \sum ||F_o| - |F_c||/\sum |F_o|$) was 0·039 for the 1172 reflexions. Atomic scattering factors were taken from Cromer & Mann (1968) and Stewart, Davidson & Simpson (1965). The final position and temperature parameters are given in Table 2.* Further details of the structure determination are given in Stothart (1973).

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* The structure factors have been deposited with the National Lending Library as Supplementary Publication SUP 30143. Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Phases assumed during structure determination*

h k l	$|E|$	Phase	
0 2 3	3·00	0	
0 5 10	2·75	$\pi/2$	Origin defining
3 0 3	2·13	$\pi/2$	
5 5 8	2·91	$\pi/2$	Enantiomorph defining
0 4 6	2·05	0	
0 4 8	2·89	0	Calculated from above
5 0 2	2·46	π	phases by $\sum_2$ relationship
4 0 8	3·17	π	
2 4 16	2·39	$\pm \pi/2$	Symbolic phase

Table 2. *Positional and thermal parameters for dextrorotatory 2'-O-tetrahydropyranyluridine (standard deviations in the last figures quoted are given in parentheses)*

The anisotropic temperature factors are expressed in the form
$$\exp[-2\pi^2 \times 10^{-4}(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl)],$$
the isotropic temperature factor in the form
$$\exp[-2\pi^2 \times 10^{-3}U(a^{*2}h^2 + b^{*2}k^2 + c^{*2}l^2)].$$

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N(1)	0·7866 (4)	−0·0140 (3)	0·3579 (1)	216 (14)	302 (15)	351 (16)	−9 (14)	27 (13)	65 (13)
C(2)	0·6313 (5)	−0·0845 (3)	0·3818 (1)	241 (20)	377 (20)	284 (18)	7 (17)	−10 (17)	20 (16)
O(2)	0·4583 (4)	−0·0743 (3)	0·3646 (1)	235 (14)	606 (17)	396 (14)	−49 (12)	−38 (11)	153 (13)
N(3)	0·6820 (4)	−0·1676 (3)	0·4265 (1)	271 (17)	551 (20)	366 (18)	−52 (15)	−4 (13)	202 (16)
C(4)	0·8708 (5)	−0·1939 (4)	0·4477 (1)	300 (18)	454 (21)	382 (20)	33 (19)	−30(17)	114 (19)
O(4)	0·8913 (4)	−0·2727 (3)	0·4887 (1)	395 (15)	795 (20)	584 (17)	−25 (16)	−66 (14)	420 (17)
C(5)	1·0267 (5)	−0·1212 (4)	0·4188 (2)	244 (18)	480 (22)	406 (22)	39 (19)	−8 (17)	51 (19)
C(6)	0·9804 (5)	−0·0340 (3)	0·3766 (2)	254 (19)	348 (19)	369 (20)	20 (16)	−3 (16)	23 (17)
O(1')	0·8760 (4)	0·0677 (2)	0·2650 (1)	360 (13)	314 (13)	342 (12)	−51 (11)	85 (11)	−1 (10)
C(1')	0·7446 (4)	0·0860 (3)	0·3129 (1)	233 (18)	311 (18)	299 (17)	6 (14)	−13 (15)	46 (15)
C(2')	0·7774 (5)	0·2274 (3)	0·3339 (1)	268 (17)	338 (18)	347 (19)	35 (16)	−4 (15)	8 (15)
O(2')	0·6112 (3)	0·2656 (2)	0·3683 (1)	365 (14)	398 (14)	421 (13)	81 (12)	28 (12)	−28 (11)
C(3')	0·8116 (5)	0·2982 (3)	0·2755 (3)	275 (18)	310 (18)	467 (20)	4 (16)	−26 (16)	66 (17)
O(3')	0·6189 (4)	0·3160 (3)	0·2495 (1)	324 (13)	594 (17)	516 (15)	73 (13)	−50 (13)	162 (14)
C(4')	0·9331 (4)	0·1964 (3)	0·2415 (1)	383 (20)	338 (20)	407 (20)	−32 (17)	58 (16)	109 (17)
C(5')	1·1582 (6)	0·2099 (4)	0·2449 (2)	397 (21)	460 (23)	672 (28)	−8 (20)	142 (21)	128 (21)
O(5')	1·2168 (4)	0·2082 (3)	0·3054 (1)	293 (13)	660 (20)	857 (22)	−62 (15)	−71 (15)	110 (17)
O(1'')	0·6338 (5)	0·4968 (3)	0·3751 (1)	553 (19)	413 (17)	907 (21)	−1 (15)	11 (19)	−120 (16)
C(2'')	0·6460 (7)	0·3775 (3)	0·4065 (2)	551 (26)	643 (30)	518 (25)	154 (24)	−105 (22)	−236 (22)
C(3'')	0·4940 (9)	0·3695 (5)	0·4556 (2)	1049 (42)	837 (34)	494 (28)	371 (35)	−2 (28)	−24 (25)
C(4'')	0·2847 (8)	0·4009 (5)	0·4352 (2)	803 (32)	756 (32)	625 (20)	114 (29)	280 (27)	44 (27)
C(5'')	0·2830 (7)	0·5285 (5)	0·4010 (2)	644 (29)	633 (30)	805 (32)	176 (26)	102 (26)	−47 (26)
C(6'')	0·4381 (7)	0·5255 (4)	0·3526 (2)	532 (28)	470 (24)	861 (33)	108 (21)	44 (25)	125 (24)

Table 2 (cont.)

	x	y	z	U_{11}
H(13)	0·588 (8)	−0·197 (5)	0·448 (2)	80 (*)
H(15)	1·155 (7)	−0·130 (4)	0·432 (2)	71 (*)
H(16)	1·080 (7)	0·021 (4)	0·354 (2)	73 (*)
H(11′)	0·594 (*)	0·073 (*)	0·302 (*)	51 (*)
H(12′)	0·898 (*)	0·238 (*)	0·356 (*)	64 (*)
H(13′)	0·897 (*)	0·387 (*)	0·278 (*)	88 (*)
H(03′)	0·636 (8)	0·349 (5)	0·215 (2)	80 (*)
H(14′)	0·903 (*)	0·202 (*)	0·200 (*)	68 (*)
H(15′)	1·237 (*)	0·124 (*)	0·218 (*)	95 (*)
H(25′)	1·194 (*)	0·290 (*)	0·224 (*)	98 (*)
H(05′)	1·329 (8)	0·239 (5)	0·305 (2)	80 (*)
H(12″)	0·793 (*)	0·382 (*)	0·421 (*)	80 (*)
H(13″)	0·501 (*)	0·290 (*)	0·475 (*)	80 (*)
H(23″)	0·561 (*)	0·435 (*)	0·482 (*)	100 (*)
H(14″)	0·200 (*)	0·401 (*)	0·471 (*)	80 (*)
H(24″)	0·230 (*)	0·330 (*)	0·412 (*)	80 (*)
H(15″)	0·319 (*)	0·605 (*)	0·425 (*)	80 (*)
H(25″)	0·148 (*)	0·544 (*)	0·382 (*)	80 (*)
H(16″)	0·399 (*)	0·447 (*)	0·320 (*)	80 (*)
H(26″)	0·452 (*)	0·620 (*)	0·329 (*)	80 (*)

Note: Parameters marked (*) were not refined in the last cycle. The error in unrefined positional parameters is probably in the range 0·05–0·1 Å.

Fig. 2. A perspective view of dextrorotatory 2′-O-tetrahydropyranyluridine showing the conformation of the molecule and the effective thermal motion of the atoms. The temperature factors of the hydrogen atoms have been reduced to $U = 0.005$ Å².

Description of the structure

A diagram of the molecule is shown in Fig. 2 and bond lengths and angles are given in Fig. 3. The overall shape is determined by the torsion angle χ about the glycosidic bond C(1′)–N(1) and by the torsion angles about the two C–O bonds linking the ribofuranose and tetrahydropyranyl rings. Newman projections giving the orientation about these bonds are shown in Fig. 4, with the usual sign convention (Sundaralingam, 1969).

The torsion angle χ between C(1′)–O(1′) and C(6)–N(1) is +49·7°, which is in the usual range (0 to +72°) for pyrimidine nucleosides (Sundaralingam, 1969) but is different from those (+16·8 and +23·8) found in β-uridine (Green, Shiono & Rosenstein, 1971), the only other uridine ribonucleoside with an unsubstituted base whose structure has been reported.

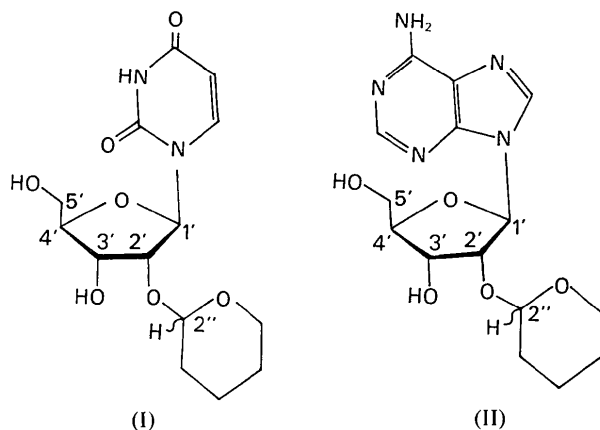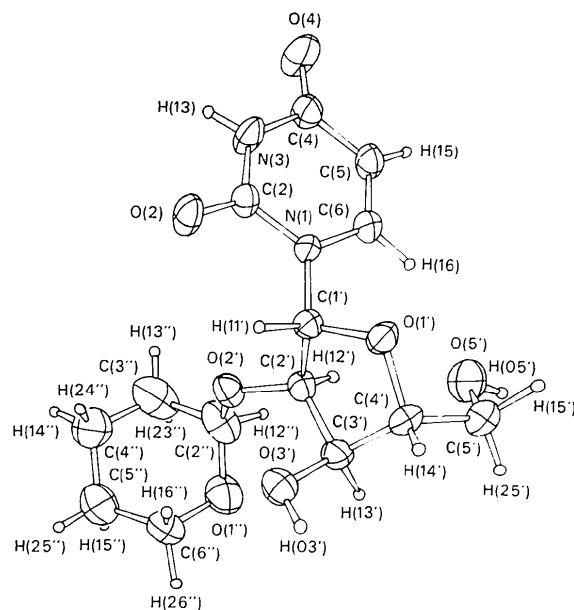(I)   (II)

Fig. 1. Structural formulae of (I) 2′-O-tetrahydropyranyl-uridine and (II) 2′-O-tetrahydropyranyladenosine.

The tetrahydropyranyl ring lies almost parallel to the plane of the uracil ring, the dihedral angle between the respective least-squares planes being 21·1°. The configuration about the acetal carbon atom of the tetrahydropyranyl ring is R in agreement with the suggestion of Klyne et al. (1967) that all the less laevorotatory tetrahydropyranyl ethers have the R absolute configuration around this atom. The S configuration was found by Kennard et al. (1971) in the more laevorotatory diastereoisomer of 2′-O-tetrahydropyranyladenosine. Despite the difference in configuration at C(2″), the shape of ThPA(−) is the same as that of ThPU(+) because the nucleoside residues are axially disposed on the tetrahydropyranyl ring in both cases, a further example of the anomeric effect. The conformation at O(2′) is that designated A1 by de Hoog, Buys, Altona & Havinga (1969).

Bond lengths and angles of the base are in the normal range for uridine derivatives. The base is significantly non-planar, being slightly folded along C(2)–C(5), with deviations of up to 0·023 Å ($= 6\sigma$) among the six atoms defining the least-squares plane (Table 3). C(1′) is even further displaced (0·088 Å) from the plane. These deviations are of the same order as those found in β-uridine, deoxyuridine (Rahman & Wilson, 1972) and 2,4-dithiouridine monohydrate (Lin & Sundaralingam, 1971) but are considerably smaller than those found in 5-chlorouridine (Hawkinson & Coulter, 1971), 5-bromouridine (Iball, Morgan & Wilson, 1966) and 4-thiouridine hydrate (Saenger & Scheit, 1970).

Table 3. *Deviations of atoms (Å) from the least-squares plane of the 6 atoms of the base ring*

N(1) (*)	0·012 (3)
C(1')	0·088 (3)
C(2) (*)	−0·023 (3)
O(2)	−0·084 (3)
N(3) (*)	0·014 (3)
H(13)	0·20 (4)
C(4) (*)	0·006 (3)
O(4)	0·042 (3)
C(5) (*)	−0·018 (4)
H(15)	0·02 (4)
C(6) (*)	0·009 (4)
H(16)	−0·01 (4)

Atoms marked (*) were used in the computation of the least-squares plane.
Equation of the least-squares plane is

$$-0.7458x + 7.365y + 15.383z = 4.8029$$

where x, y and z are in fractions of a unit cell edge in direct space.

The conformation of the ribose is C(2')-*endo* and the bond lengths and angles agree with other ribose rings having this conformation (Sundaralingam & Jensen, 1965). The deviations of the ring atoms from the best 4-atom least-squares plane is given in Table 4.
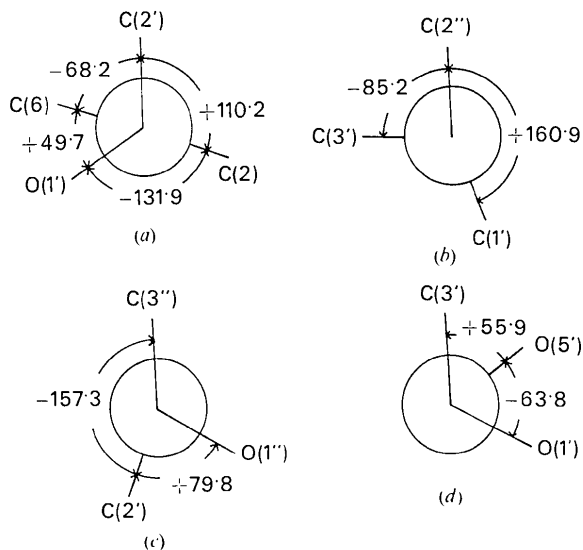

Fig. 4. Newman projections of the conformations about (a) C(1') → N(1), (b) O(2') → C(2'), (c) C(2'') → O(2'), (d) C(4') → C(5').
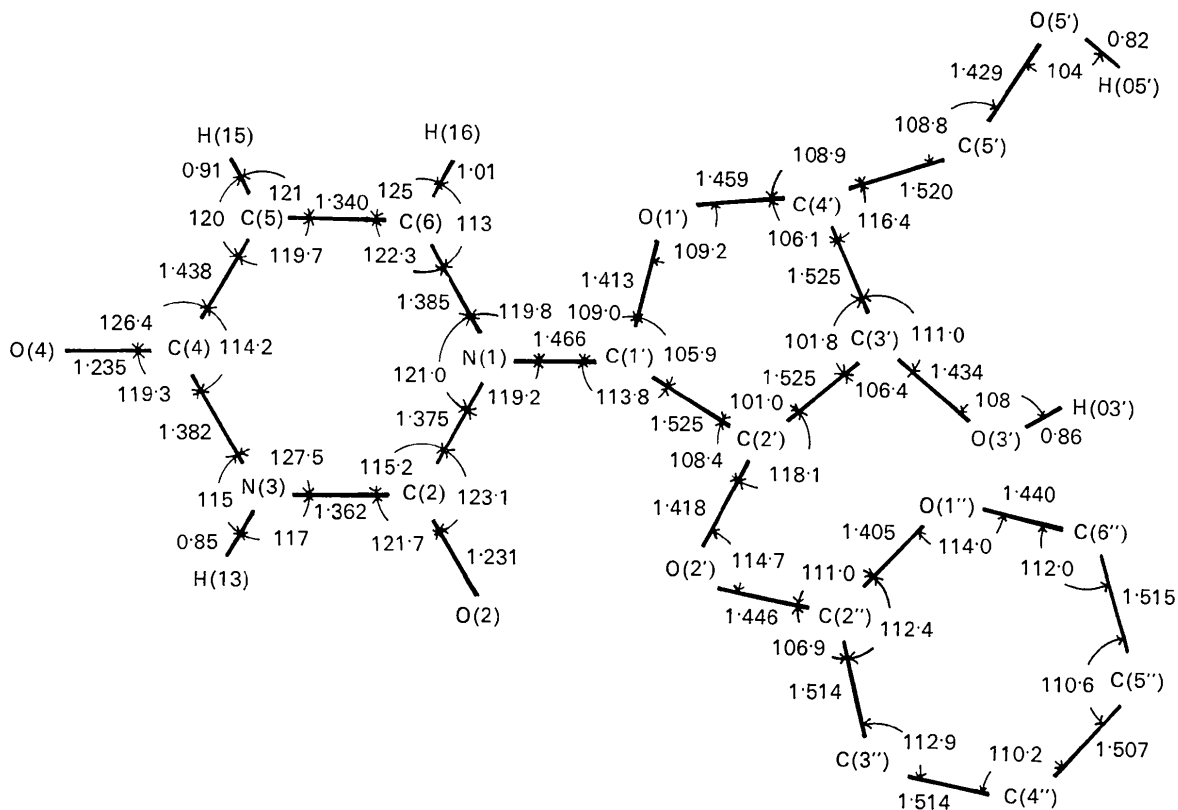

Fig. 3. Bond lengths (Å) and angles (°) in 2'-O-tetrahydropyranyluridine. Standard error in bond lengths is 0·004 Å for N–C and O–C, 0·005–0·008 Å for C–C, and 0·05 Å for N–H, O–H and C–H. Standard error in angles is 0·3° (3° for angles involving hydrogen atoms).

Table 4. *Deviations of atoms* (Å) *from the best* 4-*atom least-squares plane of the ribose ring*

O(1') (*)	−0·027 (2)
C(1') (*)	0·017 (3)
C(2')	0·606 (3)
C(3') (*)	−0·015 (3)
C(4') (*)	0·025 (4)
C(5')	1·237 (4)
O(2')	0·291 (2)

Atoms marked (*) were used in computation of the least-squares plane. Equation of the plane in direct space is

$$5\cdot111x + 0\cdot8113y + 14\cdot624z = 8\cdot435$$

where x, y, and z are in fractions of a unit cell edge in direct space.
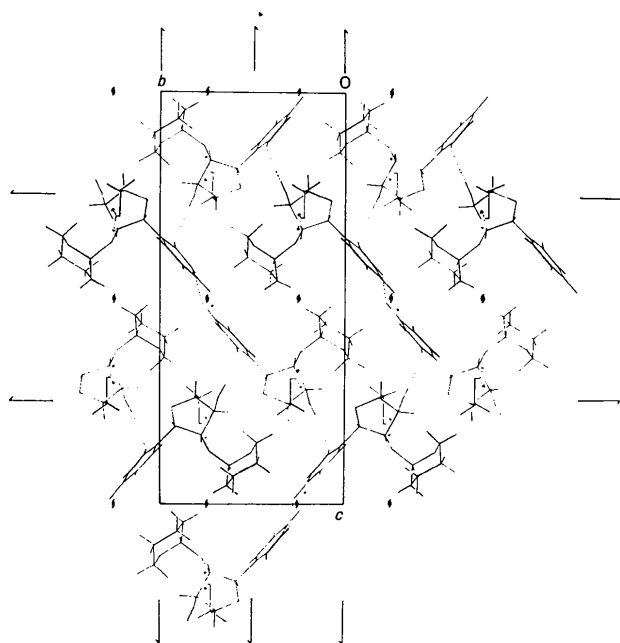

Fig. 5. Molecular packing and hydrogen bonding in 2'-O-tetrahydropyranyluridine as seen in projection down **a**. Hydrogen bonds are marked with broken lines.
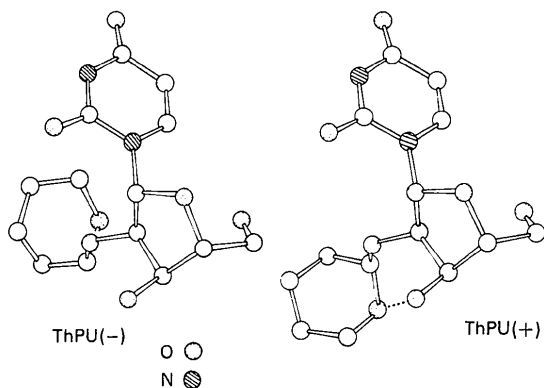

Fig. 6. (*a*) Expected molecular structure of ThPU(−). (*b*) Molecular structure of ThPU(+) with a possible intramolecular hydrogen bond shown with a broken line.

The bond length O(2')–C(2'') is perhaps significantly longer (1·446 Å) than in ThPA(−) (1·421 Å), correlating with the fact that O(2') is hydrogen-bonded in ThPU(+) but not in ThPA(−). The tetrahydropyranyl ring has the same dimensions in both ThPU(+) and ThPA(−).

The hydrogen bonding and molecular packing are illustrated in Fig. 5. The molecules are strung into columns running parallel to **a** by hydrogen bonds from O(5')–H(O5') on one molecule to O(2') and O(3') in the molecule related by the *a* translation. The columns are held in pairs by hydrogen bonds from N(3)–H(13) to O(4) on the molecule related by the *a* screw axis. Finally the pairs of columns are connected by hydrogen bonds from O(3')–H(O3') to O(2) on the molecule related by the *b* screw axis. All hydrogen bonds and other contacts between non-hydrogen atoms closer than 3·6 Å are given in Table 5. Figs. 2, 5 and 6 were drawn with *ORTEP* (Johnson, 1965).

Table 5. *Intermolecular contacts* (*not involving hydrogen atoms*) *less than* 3·6 Å

O(5')···O(3'ⁱ)	3·18*	O(4)····N(3ⁱⁱⁱ)	2·81*
C(5)···O(2ⁱ)	3·19	O(4)····O(4ⁱⁱⁱ)	3·43
C(6)···O(2ⁱ)	3·25	O(4)····C(4ⁱⁱⁱ)	3·55
O(5')···O(2ⁱ)	3·55	C(5)····O(4ⁱⁱⁱ)	3·40
O(5')···O(2'ⁱ)	3·07*	C(3')····O(1'ⁱᵛ)	3·56
C(5')···O(3'ⁱ)	3·28	O(3')····C(2ᵛ)	3·57
O(5')···C(4''ⁱ)	3·57	O(3')····O(2ᵛ)	2·87*
O(4)····C(5'''ⁱⁱ)	3·59	C(6'')···O(1'ᵛ)	3·43

* indicates hydrogen bonding
Roman numeral superscripts refer to the following equivalent positions relative to the coordinates given in Table 2.

i	$1+x$,	y,	z
ii	$\frac{1}{2}+x$,	$\frac{1}{2}-y$,	$1-z$
iii	$\frac{1}{2}+x$,	$-\frac{1}{2}-y$,	$1-z$
iv	$2-x$,	$\frac{1}{2}+y$,	$\frac{1}{2}-z$
v	$1-x$,	$\frac{1}{2}+y$,	$\frac{1}{2}-z$

Discussion

The lower polarity observed in the more dextrorotatory isomers of tetrahydropyranyl nucleosides suggests that these are better able to form intramolecular hydrogen bonds in non-polar solvents. Since this effect is observed for several different nucleosides it is probably related to the absolute configuration at C(2'') rather than to the nature of the base.

Both the crystal and molecular structures of ThPU(+) and ThPA(−) are surprisingly similar, considering the major chemical differences between them. Both crystallize in the same space group and have very similar cell dimensions. In both crystals, bases related by the screw axis parallel to the shortest edge of the unit-cell are hydrogen-bonded together, and the molecules are similarly disposed relative to the other symmetry elements. In both molecules the torsion angles [except that around O(2')–C(2'')] determining the overall shape of the molecule are similar, the tetrahydropyranyl ring being in the chair conformation and the

nucleoside residue in the axial position on it. The principal difference, apart from the base, lies in the disposition of the tetrahydropyranyl ring with respect to the O(2')–C(2'') bond. This amounts to an interchange of the C(3'') and O(1'') atoms and a rotation of 90° about C(2'') → O(2'). We may assume that the tetrahydropyranyl ring in the more laevorotatory isomer of ThPU will have a similar disposition to that in ThPA(−) so that ThPU(−) would have the molecular structure shown in Fig. 6. A comparison of the pictures of the two isomers (Fig. 6) shows that ThPU(+) can form an internal hydrogen bond [O(3')–H(O3')–O(1'')] with very little distortion of the molecule, the distance O(3')–O(1'') in the crystal being only 3·4 Å. By contrast, in ThPU(−), a large rotation would be necessary to bring O(3') and O(1'') within hydrogen-bonding distance, and such rotation would lead to unacceptably short atomic contact distances, especially between H(12'') and H(11') or O(3'). Thus in a non-polar solvent, ThPU(+) is able to present a less polar exterior than ThPU(−) with the resultant observed differences in their physical properties.

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The Crystal Structure of Hexalead Pentaborate, 6PbO.5B$_2$O$_3$

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Hexalead pentaborate, 6PbO.5B$_2$O$_3$, is triclinic with the following unit-cell dimensions at 22°C: a = 6·833 ± 0·002, b = 7·010 ± 0·002, c = 11·125 ± 0·002 Å, α = 85·89 ± 0·03, β = 102·00 ± 0·02, γ = 119·56 ± 0·02°. The space group is $P\bar{1}$ with one formula unit in the cell and a calculated density of 6·183 g cm^{-3}. Three-dimensional X-ray intensity data were measured with a Picker automatic single-crystal diffractometer and Mo $K\alpha$ radiation. The structure was determined by the heavy-atom method. A full-matrix least-squares refinement resulted in an R value of 0·065. The structure contains isolated B$_{10}$O$_{21}^{12-}$ polyions. These ions are built up from two diborate groups linked by two BO$_3$ triangles. The lead atoms are covalently bonded to oxygen, as evidenced by the short lead–oxygen distances (2·23 Å and upwards) as well as the asymmetric coordination of the lead atoms.

Introduction

The system lead oxide–boron oxide exhibits two phases of unusual stoichiometry. Geller & Bunting (1937) reported the existence of 1:2, 5:4, 2:1 and 4:1 phases in this system. Bauer & Plötscher (1967) claimed to

have found in addition 1:1 and 9:8 phases Crystalline compounds with the 5:4 and 9:8 stoichiometric ratios of metal oxide to boron oxide have not been found for other borate systems. The present investigation was undertaken to study the nature of the phase which Bauer & Plötscher believed to be a 9PbO.8B$_2$O$_3$ com-