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C—H···O Interactions and Stacking of Water Molecules between Pyrimidine Bases in 5-Nitro-1-(β-D-ribosyluronic acid)–Uracil Monohydrate [1-(5-Nitro-2,4-dioxopyrimidinyl)-β-D-ribofuranoic Acid Monohydrate]: A Neutron Diffraction Study at 80 K*

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Abstract

A low-temperature neutron diffraction study of the title compound has been carried out [$C_9H_9N_3O_9.H_2O$, $P2_1$, $Z = 2$, $a = 8{\cdot}935$ (1), $b = 10{\cdot}223$ (2), $c = 6{\cdot}530$ (1) Å, $\beta = 93{\cdot}32$ (1)°, at $T = 80$ K]. The unweighted R value based on F^2 for 1602 reflections is 0·049. The present neutron diffraction analysis has resulted in the definitive characterization of the hydrogen-bonding scheme in this material. All C—H, N—H and O—H covalent bond distances have been determined with precision better than 0·006 Å. The water molecules stack between pyrimidine bases, and the entire structure consists of layers nearly perpendicular to the c axis. The water molecules are each connected by means of O—H···O hydrogen bonds to three nucleoside molecules from neighboring stacks in approximately trigonal fashion, thus producing a 'slip-sandwich' type of arrangement. There is no direct hydrogen bonding along individual stacks. The presence of an unusually short intramolecular C—H···O hydrogen bond involving the proton on C(6) of uracil has been confirmed [H(C6)···O(5′) 2·080 (6) Å; C(6)—H(C6)···O(5′) 155·7 (4)°]. This interaction, which stabilizes the *anti* conformation of the nucleoside, may be enhanced by polarization of

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the C(6)—H(C6) bond due to the electron-withdrawing nitro group on C(5). An interesting feature of the present structure is the involvement of all protons attached to sp^3 carbons of the furanose ring in short contacts with neighboring O atoms. In particular, the environment of H(C3′) can be described as involving a bifurcated interaction [H(C3′)···O(5*B*) 2·334 (5), H(C3′)···O(2′) 2·358 (5) Å].

Introduction

The general features of the crystal structure of 5-nitro-1-(β-D-ribosyluronic acid)–uracil monohydrate, in which water molecules stack between pyrimidine bases, have been elucidated from X-ray diffraction data collected at ambient temperature (Srikrishnan & Parthasarathy, 1976, 1978). Based upon the observed stacking pattern, Srikrishnan & Parthasarathy (1976) have suggested that under certain circumstances intercalation of water molecules might stabilize extrahelical configurations in nucleic acids. In order to understand the molecular-packing scheme in this crystal better and to study the hydrogen bonding in some detail, we have refined the structure with single-crystal neutron diffraction data measured at 80 K and have accurately determined the positions of all H atoms.

Data collection

The sample of the title compound used in this work was obtained by the addition of concentrated HNO_3 to an aqueous solution of uridine, followed by slow evaporation of the resulting solution. The crystal selected had a volume of 0·62 mm³. It was mounted on an aluminum pin, the end of which was hollow to reduce the amount of metal in the neutron beam, and was oriented along the crystallographic *b* axis. The sample was placed in a liquid-nitrogen-cooled cryostat and mounted on an automated four-circle diffractometer (Dimmler, Greenlaw, Kelley, Potter, Rankowitz & Stubblefield, 1976; McMullan, Andrews, Koetzle, Reidinger, Thomas & Williams, 1976) at the Brookhaven High Flux Beam Reactor. A germanium monochromator was used with the (220) plane in transmission geometry, to produce a neutron beam of wavelength 1·1598 Å (based upon observed positions of Al_2O_3 powder lines).* During the period of data collection, the temperature of a copper block in direct contact with the aluminum sample mount was measured to be 80·0 ± 0·5 K. Cell dimensions refined by a least-squares procedure based on setting angles of 29 reflections are listed in Table 1. Intensities were measured for reflections in four octants of reciprocal space ($hkl,\bar{h}kl,h\bar{k}l,\bar{h}\bar{k}l$) with ($\sin\theta/\lambda$) $< 0·68$ Å^{-1}, employing a $\theta/2\theta$ step-scan technique. The scan range was varied according to $\Delta 2\theta = 1·17°(1·0 + 2·88) \tan\theta$ for the high-angle reflections ($60° < 2\theta < 103°$) and $\Delta 2\theta = 2·4°$ for the low-angle reflections. The step size was adjusted to give approximately 60 points in each scan. At each step, counts were accumulated for about four seconds, with the exact intervals being determined by monitoring the incident neutron flux. As a general check on experimental stability, the intensities of two reflections were remeasured every 100 reflections. These did not vary to any significant degree during the entire period of data collection.

Table 1. *Crystal data for* 5-*nitro*-1-(β-D-*ribosyluronic acid*)–*uracil monohydrate*

	295 K*	80 K	Δ
a	8·982 (1) Å	8·935 (1) Å	−0·047 (1) Å
b	10·245 (1)	10·223 (2)	−0·022 (2)
c	6·651 (1)	6·530 (1)	−0·121 (1)
β	92·27 (1)°	93·32 (1)°	+1·05 (1)°
V	611·5 (1) Å³	595·5 (1) Å³	−16·0 (2) Å³
D_c ($Z = 2$)	1·744 Mg m⁻³	1·791 Mg m⁻³	
Space group	$P2_1$	$P2_1$	
μ†		0·1423 mm⁻¹	

* Srikrishnan & Parthasarathy (1976).

† Mass-absorption coefficients of C, N and O were obtained from *International Tables for X-ray Crystallography* (1968). For H, 2390 mm² g⁻¹ was used for the effective mass absorption coefficient due to incoherent scattering, corresponding to an incoherent cross section of 40 barn (4000 fm²).

Data reduction and refinements

Integrated intensities of reflections were obtained by a modification of the Lehmann & Larsen (1974) method, with a program that employs an interactive CRT display (Takusagawa, 1977). Absorption corrections for observed intensities were made by means of numerical integration over a Gaussian grid of points (Busing & Levy, 1957). The standard deviation of each reflection was estimated as follows: $\sigma^2(F^2) = \sigma^2_{\text{count}} + 0·258 \times 10^{-2} F^4 - 0·937 \times 10^{-9} F^8$. All quantities are on an absolute scale with F^2 in barn and the constants $0·258 \times 10^{-2}$ and $-0·937 \times 10^{-9}$ were estimated from the discrepancies between symmetry-related reflections. The agreement factor, R_c, obtained on averaging the symmetry-related reflections is:

$$R_c = \sum \left(\sum_{i=1}^{n} |\langle F_o^2 \rangle - F_{oi}^2| \right) \Big/ \sum n \langle F_o^2 \rangle = 0·043.$$

The atomic coordinates of non-hydrogen atoms from the X-ray determination (Srikrishnan & Parthasarathy, 1978) were used as initial values for the present refinement. After a few cycles, a difference scattering-density synthesis showed all H atom positions. All parameters

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* Hexagonal, $a = 4·758$, $c = 12·991$ Å.

including coherent neutron-scattering lengths of N atoms and a type I isotropic extinction correction parameter (Becker & Coppens, 1975) were refined alternately in two large blocks, each containing 220 out of the total of 301 variable parameters. Parameter shifts in the final cycles were in all cases less than $0{\cdot}2\sigma$. The least-squares procedure minimized $\sum w(F_o^2 - k^2F_c^2)^2$ and used a modified version of the program by Busing, Martin & Levy (1962). Weights were chosen as $w = 1/\sigma^2(F_o^2)$. The most significant extinction correction value applied to F_c^2 was 0·731 for the reflection 002. The data collection and structure-refinement procedures are summarized in Table 2, while final positional parameters are listed in Table 3. Neutron-scattering lengths used for C, H and O atoms are $b_C = 6{\cdot}648$, $b_H = -3{\cdot}740$ and $b_O = 5{\cdot}803$ fm (Shull, 1972). The refined values for N were found to be 9·27 (8), 9·11 (8), and 9·17 (8) fm.* A final difference synthesis was found to be essentially featureless.

Table 2. *Experimental and refinement parameters*

Crystal weight	1·08 mg
Crystal volume (room temperature)	0·62 mm^3
Number of faces* $\left\{\begin{matrix}(00\bar{1}), (\bar{1}00), (0\bar{1}0)\\(001), (7\bar{8}0), (100)\\(530), (\bar{7}80)\end{matrix}\right\}$	8
Number of reflections measured	3298
Number of independent reflections	1602
$R(F^2) = \sum\lvert F_o^2 - k^2F_c^2\rvert/\sum F_o^2$	0·049
$wR(F^2) = (\sum w\lvert F_o^2 - k^2F_c^2\rvert^2/\sum wF_o^4)^{1/2}$	0·076
$s\dagger = [\sum w(F_o^2 - k^2F_c^2)^2/(m-n)]^{1/2}$	1·181

* Unusually large indices were assigned for three of the faces [$(7\bar{8}0)$, (530), and $(\bar{7}80)$], in an attempt to describe the somewhat irregularly shaped sample as accurately as possible.

† m is the number of reflections and n is the number of variable parameters (301).

Table 3. *Fractional atomic coordinates*

	x	y	z
O(2)	−0·9027 (2)	−0·1340	−0·1966 (3)
O(4)	−0·4180 (2)	−0·0307 (3)	−0·2909 (4)
O(5*A*)	−0·3347 (2)	−0·4312 (3)	−0·3549 (4)
O(5*B*)	−0·2321 (2)	−0·2427 (3)	−0·3016 (3)
O(1′)	−0·8156 (2)	−0·4886 (3)	−0·0870 (3)
O(2′)	−0·9924 (2)	−0·4210 (3)	−0·5741 (3)
O(3′)	−1·1038 (2)	−0·6062 (3)	−0·3055 (3)
O(5′)	−0·5914 (2)	−0·6410 (3)	−0·2066 (4)
O(5″)	−0·7202 (2)	−0·8228 (3)	−0·1506 (4)
O(*W*)	−0·3415 (2)	−0·7659 (3)	−0·2004 (3)
N(1)	−0·7455 (1)	−0·3033 (2)	−0·2662 (2)
N(3)	−0·6582 (1)	−0·0877 (2)	−0·2424 (2)
N(C5)	−0·3413 (1)	−0·3133 (2)	−0·3203 (2)
C(2)	−0·7776 (2)	−0·1713 (2)	−0·2318 (3)
C(4)	−0·5106 (2)	−0·1181 (2)	−0·2786 (3)
C(5)	−0·4875 (2)	−0·2577 (2)	−0·2980 (3)
C(6)	−0·6038 (2)	−0·3428 (2)	−0·2921 (3)
C(1′)	−0·8630 (2)	−0·4024 (2)	−0·2463 (3)
C(2′)	−0·8921 (2)	−0·4866 (2)	−0·4372 (3)
C(3′)	−0·9497 (2)	−0·6141 (2)	−0·3455 (3)
C(4′)	−0·8526 (2)	−0·6206 (2)	−0·1437 (3)
C(5′)	−0·7137 (2)	−0·7052 (2)	−0·1665 (3)
H(O2′)	−1·0188 (5)	−0·4785 (5)	−0·6895 (6)
H(O3′)	−1·1473 (5)	−0·5249 (5)	−0·3475 (8)
H(O5′)	−0·4991 (4)	−0·6984 (4)	−0·2114 (7)
H1(O*W*)	−0·2496 (5)	−0·7255 (5)	−0·2399 (7)
H2(O*W*)	−0·3375 (5)	−0·8589 (5)	−0·2120 (8)
H(N3)	−0·6809 (4)	0·0097 (5)	−0·2193 (7)
H(C6)	−0·5857 (5)	−0·4473 (5)	−0·3034 (7)
H(C1′)	−0·9644 (4)	−0·3480 (4)	−0·2105 (6)
H(C2′)	−0·7845 (4)	−0·5098 (5)	−0·5070 (6)
H(C3′)	−0·9329 (4)	−0·7002 (4)	−0·4422 (6)
H(C4′)	−0·9161 (4)	−0·6645 (4)	−0·0234 (6)

Discussion

Covalent-bond distances and angles from the present neutron study are shown in Fig. 1. These bonding

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34177 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

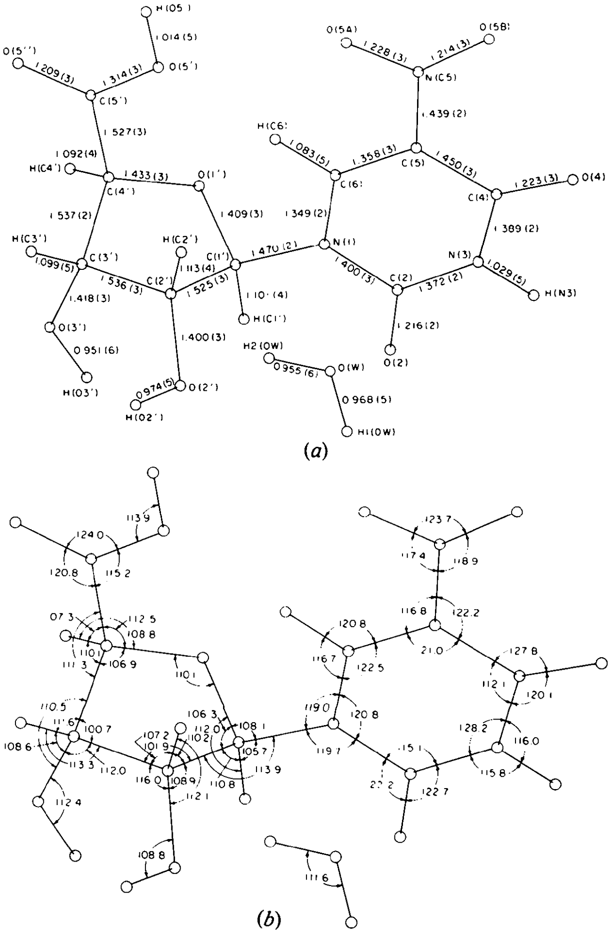

Fig. 1. (*a*) Bond distances at 80 K. Estimated standard deviations are 0·002–0·003 Å for C–C, C–O, C–N and N–O bonds, and 0·004–0·006 Å for C–H and O–H bonds. (*b*) Bond angles at 80 K. Estimated standard deviations are 0·1–0·3°.

Table 4. *Least-squares plane defined by* C(2), N(3), C(5) *and* C(6) *and deviations from the plane*

$$-0{\cdot}1300X + 0{\cdot}0975Y - 0{\cdot}9867Z = 2{\cdot}2184$$

X, Y and Z are parallel to the crystallographic a, b and c^* axes in Å.

N(1)	0·045 (2)	C(1′)	−0·045 (3)
C(2)	−0·006 (4)	O(2)	−0·048 (5)
N(3)	0·006 (3)	H(N3)	−0·018 (8)
C(4)	0·036 (3)	O(4)	0·094 (4)
C(5)	−0·006 (4)	N(C5)	−0·090 (6)
C(6)	0·006 (4)	H(C6)	−0·047 (8)

Table 5. *Torsion angles* (°) *in the* β-D-*furanosyl ring*

Values were calculated according to the IUPAC–IUB Commission on Biochemical Nomenclature (1970).

O(1′)–C(1′)–C(2′)–C(3′)	33·6 (1)
C(1′)–C(2′)–C(3′)–C(4′)	−36·2 (1)
C(2′)–C(3′)–C(4′)–O(1′)	28·0 (1)
C(3′)–C(4′)–O(1′)–C(1′)	−7·8 (1)
C(4′)–O(1′)–C(1′)–C(2′)	−16·4 (1)
O(1′)–C(1′)–C(2′)–O(2′)	156·6 (1)
H(C1′)–C(1′)–C(2′)–H(C2′)	158·1 (2)
O(2′)–C(2′)–C(3′)–O(3′)	−36·9 (1)
H(C2′)–C(2′)–C(3′)–H(C3′)	−39·8 (2)
H(C3′)–C(3′)–C(4′)–H(C4′)	−93·4 (2)
H(C4′)–C(4′)–O(1′)–C(1′)	−126·6 (1)
C(4′)–O(1′)–C(1′)–H(C1′)	104·8 (1)

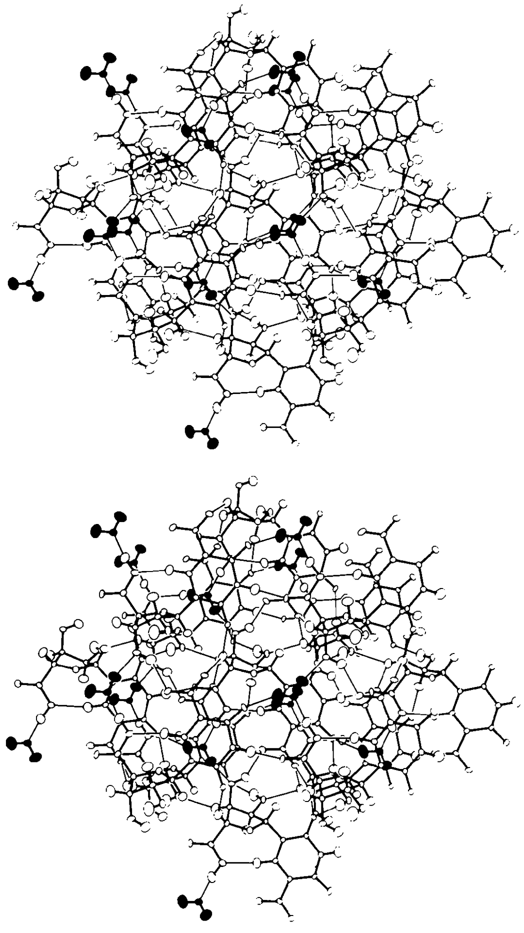

Fig. 2. Stereoscopic view of the crystal structure down the c^* axis. The a axis is horizontal. Thin lines indicate hydrogen bonds and short contacts, and the water molecules have been filled in for clarity.

parameters agree quite well with those determined by X-ray diffraction and cited by Srikrishnan & Parthasarathy (1978), except for the expected discrepancies in positions of the H atoms. The pyrimidine ring deviates slightly from planarity (Table 4) in such a way as to form a twisted boat. The furanose ring has the C(2′)-*endo*-C(3′)-*exo* ($^2T_3$) conformation, with the torsion angles listed in Table 5.

The general features of the structure have been discussed by Srikrishnan & Parthasarathy (1976, 1978). The discussion here will mainly be focused on the observed hydrogen-bonding scheme and on aspects of the structure which are found to change upon lowering the temperature of the crystal.

The crystal structure is illustrated in Fig. 2 (Johnson, 1976). The water molecules stack between pyrimidine bases, as has been mentioned earlier. The planes of the water molecules and of the bases are nearly parallel to one another, and almost perpendicular to c^*. In the view shown in Fig. 2, each water molecule lies 3·014 Å from the base above it, and 3·371 Å from that below. These displacements are similar to base-stacking distances observed in nucleic acid polymers and crystals of monomers (Bugg, Thomas, Sundaralingam & Rao, 1971).

Details of the hydrogen-bonding scheme in the present structure are shown in Fig. 3. As can be seen in Fig. 3(*a*), the water molecules are each held in place by three hydrogen bonds. This produces a 'slip-sandwich' type of arrangement, in which each water molecule is connected to three nucleoside molecules from neighboring stacks, in approximately trigonal fashion. There is no direct hydrogen bonding along c^* connecting adjacent water and nucleoside molecules belonging to the same stack, although a weak contact of 2·671 (6) Å exists between H2(O*W*) and O(1′). The angle which the O(*W*)···H(O5′) hydrogen bond makes with the normal to the plane of the water molecule is 69·0°, and the water molecule is thus type-*F* according to the classification of Chidambaram, Sequeira & Sikka (1964): the bisector of the lone pairs of the O atom is directed approximately towards the donor H(O5′). [The same situation occurs for the three hydroxyl groups in this structure, since the angles around the O atoms in question sum to more than 358° in each case, as can be seen in Fig. 3(*a*)–(*c*).]

The *anti* conformation of the nucleoside is stabilized by an intramolecular C—H···O hydrogen bond joining the uracil C(6) atom with the carboxyl group [see Figs. 3(*b*) and 4(*a*)]. The H(C6)···O(5′) distance of

2·080 (6) Å is over 0·3 Å shorter than the sum of van der Waals radii for H and O atoms (2·4 Å), if the van der Waals radius of H in a polar environment is taken to be 1·0 Å as recommended by Baur (1972). An intermolecular C—H···O bond involving C(6), similar in length to that observed here [H···O 2·045 (3) Å], has been found to exist in crystalline 1-methylthymine (Kvick, Koetzle & Thomas, 1974). In the present structure, the intramolecular C—H···O interaction may be enhanced by polarization of the C(6)—H(C6) bond due to the electron-withdrawing nitro group on C(5). In addition to the intramolecular C(sp^2)—H···O bond, all protons attached to sp^3 C atoms of the furanose ring are engaged in short contacts with neighboring O atoms. The environment of H(C3′), shown in Fig. 3(*c*), can clearly be described as involving a bifurcated interaction (Parthasarathy, 1969; Koetzle, Hamilton & Parthasarathy, 1972). The H···O distances in question are very similar, and the four atoms C(3′), H(C3′), O(2) and O(5*B*) almost lie in a plane [the sum of bond angles about H(C3′) totals 358·9°]. In the case of H(C4′), illustrated in Fig. 3(*d*), the contact with O(2) is much shorter than that with O(5*B*), and the latter interaction occurs within the range of normal van der Waals distances. H(C2′) is involved in a short contact with O(4) from a neighboring molecule, as shown in Fig. 3(*a*). Finally, H(C1′) has an intramolecular contact of 2·256 (4) Å with O(2). However, the C(1′)—H(C1′)···O(2) and H(C1′)···O(2)—C(2) angles are 107·3 (2) and 85·0 (1)° respectively, and this latter angle is especially unfavorable for hydrogen-bond formation.

Each nucleoside molecule is joined to three neighboring nucleosides, by means of hydrogen bonds H(O3′)···O(5*A*),† H(O2′)···O(2), and H(N3)···O(5″), in addition to being joined to three water molecules by H(O5′)···O(*W*), O(3′)···H1(O*W*) and O(4)···H2(O*W*). All these N—H···O and O—H···O bonds are used to form the molecular sheets oriented perpendicular to *c**, except for H(O2′)···O(2), which connects nucleoside molecules in adjacent sheets that are related by a screw axis. Adjacent sheets are also joined by the weak C—H···O interactions involving the furanose ring protons.

Stacking of pyrimidine bases and water molecules, similar to that occurring in the present structure, has also been found to take place in 1-methyl-5-nitrouracil monohydrate (Ginell & Parthasarathy, 1977) and orotic acid monohydrate (Takusagawa & Shimada, 1973). In 1-methyl-5-nitrouracil monohydrate the water molecules are displaced further from the positions over the centroids of the pyrimidine rings than is the case here, while in orotic acid monohydrate the packing is such that a water molecule lies on top of each pyrimidine ring, but adjacent layers are shifted

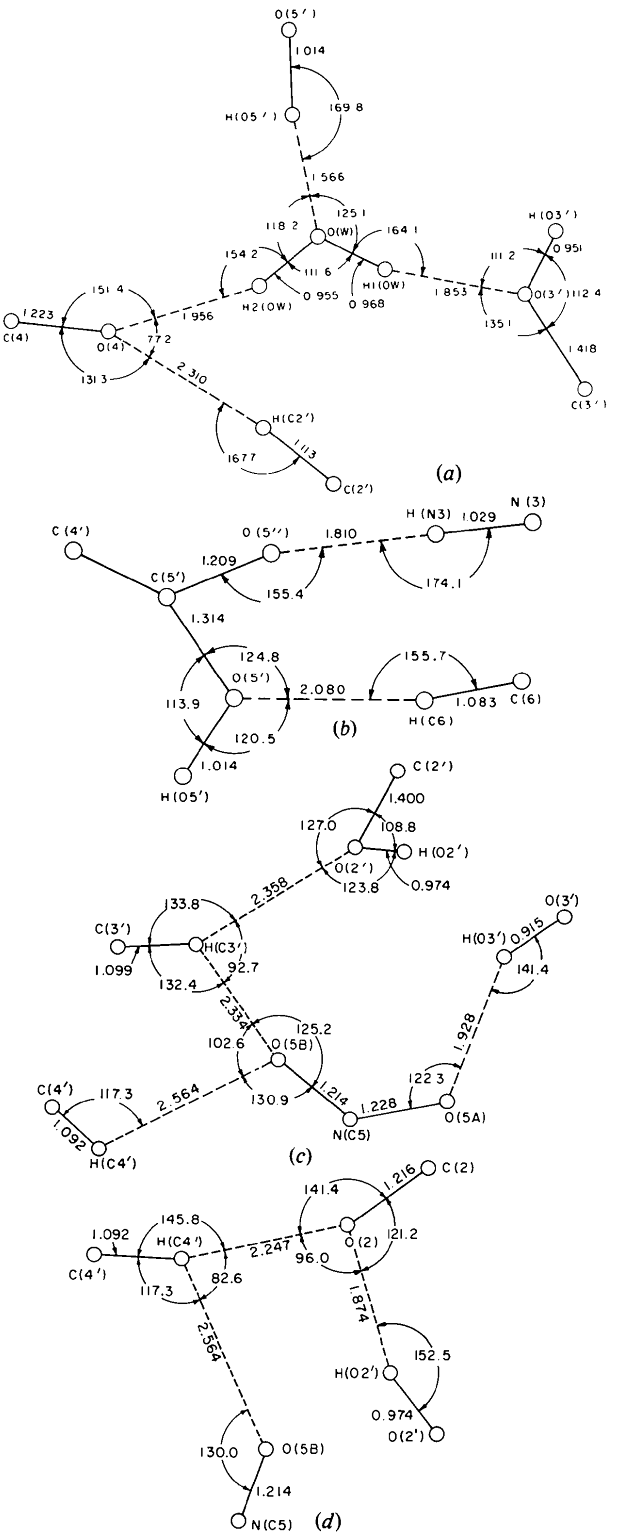

Fig. 3. Geometry of the hydrogen bonds. Estimated standard deviations are 0·004–0·006 Å for hydrogen-bond distances and 0·2–0·5° for angles. (*a*) Environment of the water molecule, (*b*) environment of the carboxyl group, including the intramolecular C—H···O hydrogen bond, (*c*) environment of H(C3′) and the nitro group, (*d*) environment of H(C4′) and O(2).

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† H(O3′) is also involved in a short intramolecular contact of 2·338 (5) Å with O(2′) [relevant angles are O(3′)—H(O3′)···O(2′) = 109·4 (4)° and H(O3′)···O(2′)—C(2′) = 76·1 (2)°].

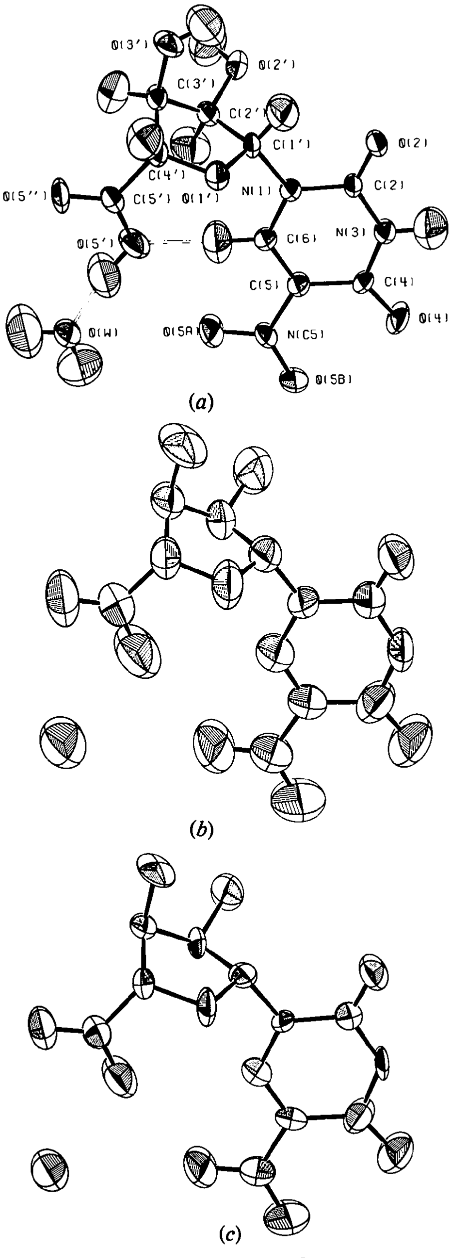


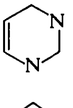
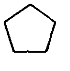
Fig. 4. (*a*) Molecular view of 5-nitro-1-(β-D-ribosyluronic acid)-uracil monohydrate at 80 K. Thermal ellipsoids are drawn at the 97% probability level. (*b*) Molecular view at 295 K. Hydrogen atoms are omitted. Thermal ellipsoids are drawn as in (*a*). (*c*) Difference thermal ellipsoids which are calculated by U_{ij}(diff.) = U_{ij}(295 K) − U_{ij}(80 K). Ellipsoids are drawn as in (*a*).

and there is no base directly above each water molecule. These types of sandwiching or stacking might be expected to confer some added stability to the structures, based on dipole–induced dipole interactions, similar to those operative in many purine and pyrimidine crystals, where in the majority of cases the bases stack with electronegative heteroatoms forming close contacts with the aromatic ring systems (Bugg *et al.*, 1971). In the present structure, it is perhaps significant that the packing is such as to orient each of the water H—O bond dipoles antiparallel to one of the C—O dipoles on 5-nitrouracil. However, this arrangement is not observed in 1-methyl-5-nitrouracil monohydrate or orotic acid monohydrate. The orientations of the water molecules are evidently determined primarily by the requirements for hydrogen-bond formation. Obviously the strongest attractive intermolecular forces in these structures are those due to hydrogen bonding, and stacking interactions of the dipole–induced dipole and dipole–dipole type are expected to be of secondary importance.

The unit-cell dimensions determined at 80 K are compared in Table 1 with those found at ambient temperature. The major change is observed in the crystallographic *c* axis, which is approximately perpendicular to the molecular sheets. The increase in the crystallographic β angle upon cooling, 1·05 (1)°, may be due to a closer approach of the molecular sheets. These sheets are interconnected by one kind of O—H···O and several weak C—H···O hydrogen bonds as mentioned above. Rigid-body thermal-motion analyses† carried out by the method of Schomaker & Trueblood (1968) indicate that the largest translational tensor component is along $c^*(T_Z)$, as summarized in Table 6. All translational tensor components are markedly lower at 80 than at 295 K, as expected. In particular, the large decrease in T_Z reduces the effective 'thickness' of the molecules. This allows shorter

Table 6. *Summary of rigid-body thermal-motion analyses*

The units for mean-square amplitude of translational vibration (T) and r.m.s. fit, $\langle \Delta U^2 \rangle^{1/2}$, are 0·0001 Å^2.

Model*	Temperature	T_X	T_Y	T_Z	$\langle \Delta U^2 \rangle^{1/2}$
	80 K	63 (3)	59 (3)	214 (71)	4
	295 K	147 (13)	133 (12)	820 (265)	15
	Difference†	84 (13)	75 (12)	606 (260)	15
	80 K	69 (2)	46 (5)	137 (6)	5
	295 K	196 (74)	123 (12)	313 (14)	11
	Difference†	128 (79)	74 (13)	176 (15)	12

* The X, Y, and Z coordinate system used in these calculations is parallel to the crystallographic a, b and c^* axes.

† T and $\langle \Delta U^2 \rangle^{1/2}$ are calculated from difference thermal parameters [*i.e.* U_{ij}(diff.) = U_{ij}(295 K) − U_{ij}(80 K)].

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† The thermal parameters from the ambient temperature (295 K) X-ray diffraction study do not represent the nuclear motion but rather are related to the distribution of electronic charge. Therefore, strictly speaking, the thermal parameters determined at 295 K (X-ray) are of a different nature from those determined at 80 K (neutron). However, these differences are expected to be quite small, especially for the ring C and N atoms, since the distribution of valence electrons about these nuclei should be moderately close to spherical.

contacts between the molecular sheets, and is in turn related to the large thermal coefficient of *c*. Bond distances have been corrected for effects of rigid-body libration and for the neutron results corrected values are about 0·002 Å longer than uncorrected values for the pyrimidine ring and 0·001 Å for the furanose ring.

The thermal motions of individual atoms are illustrated in Fig. 4. Ellipsoids calculated by U_{ij}(diff.) = U_{ij}(295 K) − U_{ij}(80 K), showing the reduction in thermal motion for each atom upon cooling, are drawn in Fig. 4(*c*). These U_{ij}(diff.) values have been subjected to rigid-body thermal analyses, and results of these calculations are included in Table 6. The *T* values calculated based on U_{ij}(diff.) are in good agreement with the difference between corresponding tensor components calculated at 295 and 80 K. The difference thermal motions in Fig. 4(*c*) are quite reasonable for all atoms except possibly in the case of N(3), where the difference term is quite markedly anisotropic.

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The Crystal Structures of 2-Aminophenol and 2-Amino-4-chlorophenol

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Abstract

The crystal structures of 2-aminophenol (I) and 2-amino-4-chlorophenol (II) have been determined from visually estimated Weissenberg data using unfiltered Cu *K* radiation. Crystals of (I) are orthorhombic, space group *Pbca*, with *a* = 7·256 (3), *b* = 7·849 (6), *c* = 19·754 (6) Å. Crystals of (II) are monoclinic, space group $P2_1/c$, with *a* = 11·226 (12), *b* = 7·374 (9), *c* = 8·011 (10) Å, β = 105·8 (3)°. Structure (I) was solved by direct methods and refined by full-matrix least-squares calculations to a final *R* of 11·0% for 693 reflexions; structure (II) was solved by Patterson and electron-density maps and refined by full-matrix least-squares calculations to a final *R* of 10·0% for 807 reflexions. In both structures the molecules are held together by two types of hydrogen bonds forming sheets, and these sheets are held together by weak van

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