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A Novel Intercalation of a Water Molecule Between Pyrimidine Bases in 5-Nitro-1-(β-D-ribosyluronic acid)–Uracil Monohydrate [1-(5-Nitro-2,4-dioxopyrimidinyl)-β-D-ribofuranuronic Acid Monohydrate]*

BY T. SRIKRISHNAN AND R. PARTHASARATHY†

Center for Crystallographic Research, Roswell Park Memorial Institute, Buffalo, NY 14263, *USA*

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Abstract. $C_9H_9N_3O_9.H_2O$, monoclinic, $P2_1$, a = 8·982 (1), b = 10·245 (1), c = 6·651 (1) Å, β = 92·27 (1)° at 22 ± 3°C, V = 611·5 Å^3, Z = 2, FW 321, λ(Cu $K\alpha$) = 1·54051 Å, D_m (flotation) = 1·74, D_x = 1·75 g cm^{-3}, μ(Cu $K\alpha$) = 7·6 cm^{-1}, R = 0·056. The molecule exhibits *anti* conformation (χ_{CN} = 53·9°), an intramolecular C(6)—H···O(5′) hydrogen bond and C(2′)-*endo*, C(3′)-*exo* ($^2T_3$) pucker. Two unusual features in this structure are (*a*) the intercalation of water molecules between stacked pyrimidine rings 6·55 Å apart and related by the **c** translation and (*b*) a number of C—H···O interactions.

Introduction. In connection with a project on radiation sensitization, we have been investigating a series of nitro-substituted bases and nucleosides. Our interest in these structures was to study the hydrogen-bonding scheme of these modified nucleosides as well as to correlate the orientation of the '**g**' tensor of these nitro radicals (analysis in progress by Dr H. Box of this Institute) using spin resonance techniques.

The title compound (I) was first synthesized by Fox and co-workers (Wempen, Doerr, Kaplan & Fox, 1960) in the course of their screening of nitro analogs of nucleosides for possible antitumour activities. Crystals of the title compound were obtained by the addition of conc. HNO_3 to the aqueous solution of uridine, followed by slow evaporation of the resulting solution. The unit-cell and other crystallographic data are given in the *Abstract*. 1438 reflections (only nine had intensities $<2\sigma$) to the limit of 2θ = 165° for Cu $K\alpha$ were collected using the stationary-crystal–stationary-counter procedure (Furnas & Harker, 1955) and were processed in the usual way. A detailed absorption correction depending on the shape of the crystal (Coppens, 1970) was carried out.

The structure (Fig. 1) was solved by a combination of *MULTAN* (Germain, Main & Woolfson, 1971) and trial-and-error methods. One of the E maps gave two

Table 1. *Atomic coordinates* (×10^4) *for the non-hydrogen atoms with e.s.d.'s in parentheses*

	x	*y*	*z*
O(2)	−9044 (3)	−1340	−2062 (5)
O(4)	−4194 (4)	−314 (4)	−2930 (7)
O(5*a*)	−3341 (4)	−4313 (4)	−3432 (10)
O(5*b*)	−2341 (4)	−2420 (4)	−2980 (7)
O(2′)	−9866 (4)	−4206 (4)	−5669 (6)
O(3′)	−11014 (4)	−6051 (4)	−2972 (7)
O(1′)	−8172 (4)	−4886 (3)	−874 (5)
O(5′)	−5929 (4)	−6404 (4)	−2014 (7)
O(5″)	−7240 (4)	−8221 (4)	−1602 (8)
O*W*	−6568 (4)	−2662 (4)	−7914 (7)
N(1)	−7450 (4)	−3033 (3)	−2631 (6)
N(3)	−6599 (4)	−886 (4)	−2476 (7)
N(C5)	−3429 (4)	−3132 (5)	−3147 (7)
C(2)	−7795 (5)	−1717 (4)	−2357 (7)
C(4)	−5118 (5)	−1182 (5)	−2781 (7)
C(5)	−4888 (4)	−2585 (5)	−2940 (7)
C(6)	−6043 (5)	−3426 (5)	−2863 (7)
C(1′)	−8635 (4)	−4028 (4)	−2458 (7)
C(2′)	−8891 (5)	−4868 (4)	−4302 (7)
C(3′)	−9479 (4)	−6124 (4)	−3402 (7)
C(4′)	−8545 (5)	−6215 (4)	−1449 (7)
C(5′)	−7151 (5)	−7047 (4)	−1715 (7)

* Stereochemistry of Nucleic Acid Components and Their Reaction Products. V. Part IV: Parthasarathy, Ohrt & Chheda (1976).

† To whom correspondence should be addressed.

Table 2. *Final atomic coordinates* ($\times 10^3$) *for the hydrogen atoms with e.s.d.'s in parentheses*

	x	*y*	*z*
H(O2′)	−990 (7)	−463 (7)	−678 (9)
H(O3′)	−1131 (6)	−564 (6)	−276 (9)
*H(O5′)	−50 (1)	−69 (1)	−29 (2)
*H1(O*W*)	−69 (1)	−29 (1)	−73 (1)
*H2(O*W*)	−70 (1)	−35 (1)	−92 (2)
H(N3)	−676 (5)	−18 (5)	−241 (7)
H(C1′)	−951 (6)	−353 (6)	−209 (8)
H(C2′)	−787 (5)	−512 (5)	−490 (8)
H(C3′)	−921 (7)	−690 (7)	−412 (9)
H(C4′)	−930 (12)	−692 (11)	−27 (16)
H(C6)	−587 (8)	−448 (8)	−315 (11)

* Not well located. *B* values for these atoms range from 6 to 12 Å^2; the coordinates are $\times 10^2$.

fragments (one of which was a six-membered ring) from which the structure was developed from difference electron-density maps and refined by the least-squares method with block-diagonal approximation to a final *R* value of 0·056 [$R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$]. The H atoms were obtained from difference electron-density maps and their parameters were refined isotropically. The refinement was carried out by minimizing $\Sigma w[|F_o| - (1/K)|F_c|]^2$, and the observations were weighted by $1/f_C$, where f_C is the scattering factor for C. Atomic scattering factors for C, N and O were taken from *International Tables for X-ray Crystallography* (1968) and for H atoms from Stewart, Davidson & Simpson (1965). The final atomic coordinates and thermal parameters are given in Tables 1 and 2. The bond distances and angles are in Fig. 1.*

Discussion. The pyrimidine ring is slightly bent into a twisted boat with displacements for N(1) and C(4) from the mean plane through the other atoms of 0·023 and 0·017 Å respectively. The nitro group is planar and inclined by 7·6° from the best mean plane through the pyrimidine ring, as compared with 4·7° for 5-nitrouracil (Craven, 1967). The molecule (Fig. 2) is in the *anti* conformation ($\chi_{CN} = 53{\cdot}9°$). The furanose ring has the C(2′)-*endo*, C(3′)-*exo* ($^2T_3$) conformation, with C(2′) and C(3′) deviating from the plane of the other three atoms by 0·418 and −0·199 Å respectively. The exocyclic O(2′) lies almost on this plane (0·026 Å), but O(3′) is displaced considerably (1·58 Å) on the side opposite to C(5′). Extending the conventional notation for nucleosides to this molecule, the values of the φ_{OO} and φ_{OC} angles are −97·9 and 20·5°; the conformation about C(4′)–C(5′) can best be described as anti-periplanar to C(3′) and synclinal to O(1′).

The hydrogen bonding and packing are illustrated in Fig. 3 and the hydrogen-bonding distances and angles are given in Table 3. The OH of the carboxyl takes part in a short O–H···O hydrogen bond to an adjacent water molecule. There is no self-association of the bases through hydrogen bonding; N(3) is hydrogen bonded to O(5″) of the carboxyl, rather than to any of the keto O atoms on the uracil base. The water molecule is at

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33226 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

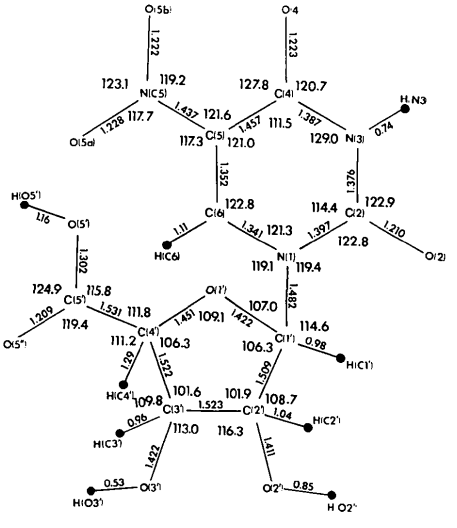

Fig. 1. Bond distances (Å) and angles (°) in the molecule. The average e.s.d.'s of bond distances and angles not involving H atoms are 0·006 Å and 0·4° respectively.

Fig. 2. The molecule in the *anti* conformation. Note the intramolecular C–H···O and the O(5′)–H(O5′)···O*W* hydrogen bonding in the structure. The torsion angles around the ribose ring, and the C(6)–N(1)–C(1′)–O(1′) and C(6)–C(5)–N(C5)–O(5*a*) torsion angles are shown.

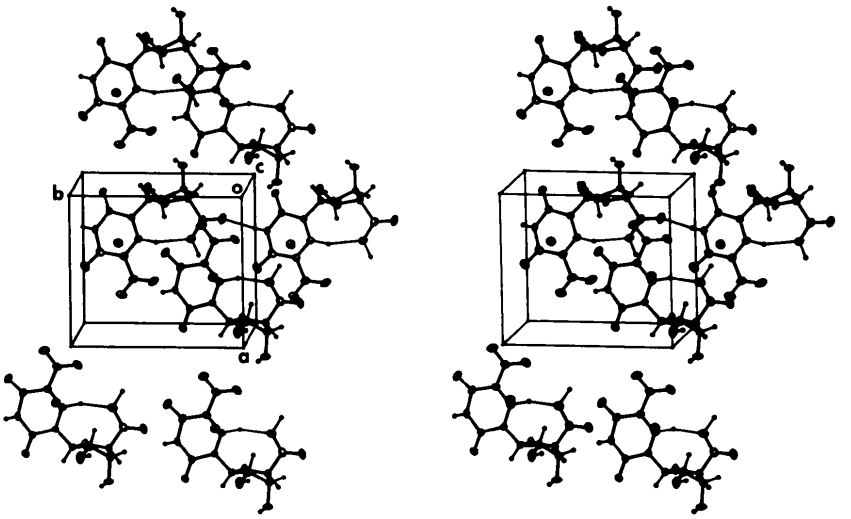

Fig. 3. A stereoview of the packing and hydrogen bonding of the molecules in the crystal structure.

Table 3. *Hydrogen bonds and weak hydrogen interactions*

D–H···*A*	*D*–H (Å)	H···*A* (Å)	*D*···*A* (Å)	∠*D*–H···*A* (°)
N(3)–H(N3)···O(5″)^{i}	0·74 (5)	2·13 (5)	2·855 (6)	168 (5)
O(2′)–H(O2′)···O(2)^{iv}	0·85 (6)	2·13 (7)	2·810 (5)	137 (6)
O(3′)–H(O3′)···O(5a)^{v}	0·53 (6)	2·30 (6)	2·754 (5)	146 (8)
O(5′)–H(O5′)···O*W*^{vi}	1·2 (1)	1·7 (1)	2·589 (5)	128 (9)
C(6)–H(C6)···O(5′)	1·11 (9)	2·11 (7)	3·104 (6)	147 (6)
C(2′)–H(C2′)···O(4)^{ii}	1·04 (5)	2·41 (5)	3·418 (6)	163 (4)
C(3′)–H(C3′)···O(2′)^{iv}	0·96 (7)	2·51 (7)	3·268 (6)	136 (5)
C(4′)–H(C4′)···O(2)^{iii}	1·29 (11)	2·27 (11)	3·251 (6)	130 (7)

The superscripts refer to the following symmetry relationships:
(i) $x, 1+y, z$; (ii) $\bar{1}-x, -\frac{1}{2}+y, \bar{1}-z$; (iii) $\bar{2}-x, -\frac{1}{2}+y, \bar{z}$; (iv) $\bar{2}-x, -\frac{1}{2}+y, \bar{1}-z$; (v) $\bar{1}+x, y, z$; (vi) $\bar{1}-x, -\frac{1}{2}+y, \bar{1}-z$.

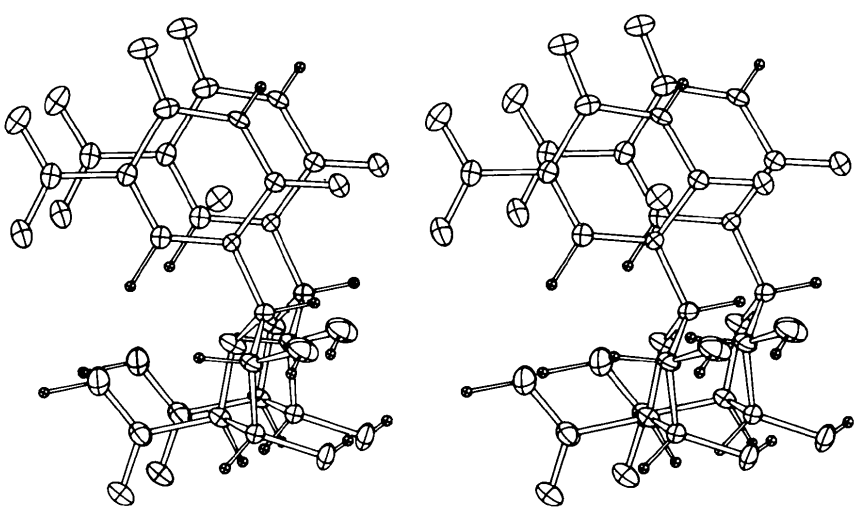

Fig. 4. A stereoview of the intercalation of the water molecule between the nucleic acid bases, viewed normal to the plane of the base.

hydrogen-bonding distances of 2·86 and 2·81 Å respectively from O(4)[$\bar{1} - x, -\frac{1}{2} + y, \bar{1} - z$] and O(3′)[$2 - x, y + \frac{1}{2}, 1 - z$] and is possibly hydrogen bonded to them [O(4)···O*W*···O(3′), 134°], but the location of the H atoms of the water is not unequivocal. Around the water O atom, two diffuse clouds of electron density (of approximately 0·3 e Å^{-3} extending up to 1 Å in the **b** direction) are present. If these densities are taken to represent the two H atoms of the water molecule and their coordinates are refined, their new orientations do not correspond to the possible hydrogen bonding involving O(3′) and O(4).

The intercalation of water between nucleic acid bases (Fig. 4) is very unusual (Srikrishnan & Parthasarathy, 1976). It is interesting to note that 5-nitrouridine monohydrate (Egert, Lindner, Hillen & Gassen, 1977) does not form a water sandwich. The water molecules are found to be nearly in the plane of nucleic acid bases (Fig. 2), as found in other related structures. In addition, they intercalate between bases in one stack of nucleic acid bases but are in the same plane as the nucleic acid bases in an adjacent stack, that is shifted, vertically relative to the first stack, by approximately 3·2 Å.

The occurrence of a C(sp^2)–H···O hydrogen bond (Table 3) [C(6)–HC(6)···O(5′)] in this structure is noteworthy. The presence of an 'electron-withdrawing' nitro group adjacent to C(6)–H causes additional polarization of this bond and enables this H to take part in a hydrogen bond. In addition, there are three C(sp^3)–H···O interactions (Table 3) involving the ribose C atoms. These interactions are unexpected since these contacts involve C(sp^3)–H and not C(sp^2)–H bonds.

The contacts from H(C2′) and H(C4′) (Table 3) are of the order of the sum of the van der Waals radii of H and O. The distances and angles involved (Table 3) indicated some attractive interaction between the C(sp^3)–H and the potential hydrogen-bond acceptors.

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The Structure of *p*-Dimethylaminobenzoic Acid

BY MEENAKSHI VYAS, T. D. SAKORE AND A. B. BISWAS

Department of Chemistry, Indian Institute of Technology, Bombay 400076, *India*

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Abstract. $C_9H_{11}NO_2$, triclinic, $P\bar{1}$, $a = 8{\cdot}598\ (7)$, $b = 8{\cdot}061\ (7)$, $c = 6{\cdot}652\ (8)$ Å; $\alpha = 66{\cdot}099\ (6)$, $\beta = 94{\cdot}62\ (5)$, $\gamma = 90{\cdot}97\ (5)°$, $D_m = 1{\cdot}29$, $D_x = 1{\cdot}31$ g cm^{-3}, $Z = 2$. The structure was determined from three-dimensional X-ray diffraction data and refined by the least-squares method to $R = 0{\cdot}113$. The dimethylamino and carboxyl groups are displaced slightly from the plane of the benzene ring and the N atom is non-planar. Pairs of molecules link together to form dimers through two O–H···O hydrogen bonds (2·622 Å) and the N atom is free from any binding of either type N–H···O or N–H···C.