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Structure of 2′,3′,5′-Tri-*O*-acetyluridine, $C_{15}H_{18}N_2O_9$

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Abstract. $M_r = 370{\cdot}3$, orthorhombic, $P2_12_12_1$, $a = 7{\cdot}493\,(5)$, $b = 14{\cdot}327\,(8)$, $c = 16{\cdot}380\,(8)$ Å, $U = 1758{\cdot}4$ Å^3, $Z = 4$, $D_x = 1{\cdot}398$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 0{\cdot}076$ mm^{-1}, $F(000) = 776{\cdot}0$, $T = 293$ K, $R = 0{\cdot}089$ for 1712 observed reflexions (Friedel pairs merged). The sugar-ring pucker is $^3T_4$ [C(3′)-*endo*/C(4′)-*exo*], with $P = 46{\cdot}5\,(6)°$, and χ_{CN}[C(2)—N(1)—C(1′)—O(4′)] is 74·2 (6)°, in the *syn* range. A close contact of 2·90 (3) Å between acetyl oxygen O(5′1) and a neighbouring base ring is noted. The pyrimidine base ring is essentially planar, as are the acetyl groups.

Introduction. This structure determination forms part of a series of such studies being undertaken in this laboratory of nucleoside analogues, including heavy-atom and acetyl substituted compounds.

Experimental. Both crystals used were small prisms, size *ca* 0·5 × 0·3 × 0·3 mm; cell dimensions by diffractometry (Stoe Stadi II diffractometer) from crystals mounted along **a** and **c**, using 20 reflexions; structure determined by direct methods using *SHELX*76 (Sheldrick, 1976); *XANADU* (Roberts & Sheldrick, 1975) and *PLUTO* (Motherwell & Clegg, 1978) program packages also used; all calculations performed on the Dundee University DEC-10 computer; data collected using the *a*-axis crystal in the range $h = 0$ to 6, $0 < 2\theta < 55°$, and the *c*-axis crystal in the range $l = 0$ to 5, $0 < 2\theta < 55°$; max. $\sin\theta/\lambda = 0{\cdot}75$ Å^{-1}; absorption corrections not applied; index range: $-9 < h < 9$, $-18 < k < 18$, $-21 < k < 21$; standard reflexion measured every 100 reflexions on each layer line, only random intensity variation (<5%) from their mean intensities; 2393 reflexions measured, $R_{\text{int}} = 0{\cdot}053$; 1712 unique reflexions [$F > 6\sigma(F)$] regarded as observed and used in analysis; all atoms except H refined by least squares (on F) using anisotropic temperature factors; a difference Fourier map revealed electron density at most of the expected H-atom positions; all H atoms except H(3) included at fixed positions based on their positions on the difference Fourier map; H(3) constrained close to its position as obtained from the difference Fourier map; H-atom temperature factors fixed at 1·5 times the isotropic value of the parent atom; final refinement involved 236 parameters, $R = 0{\cdot}089$, $wR = 0{\cdot}078$, $w = 8{\cdot}7889/[\sigma^2(F) + 0{\cdot}000535F^2]$, max. shift/e.s.d. < 0·01, $\Delta\rho$ ±0·4 e Å^{-3}; scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. The atomic numbering used is shown in Fig. 1, with atomic coordinates in Table 1.* Bond lengths and angles are listed in Table 2. The bond distances O(4′)—C(1′) [1·432 (7) Å] and O(4′)—C(4′) [1·430 (7) Å] here are, unusually, equal. As has been noted (de Kok, Romers, de Leeuw, Altona & van Boom, 1977), there are numerous examples of these bond lengths being different, O(4′)—C(1′) being on average 0·04 Å shorter than O(4′)—C(4′). This is attributed (Sundaralingam, 1975) to the delocalization of electrons from O(4′) to C(1′) antibonding orbitals. There seems no apparent reason why this effect should not be observed here.

Also worthy of note are the lengths of the acetyl carboxyl bonds, O(2′1)—C(2′1) [1·184 (9) Å], O(3′1)—C(3′1) [1·185 (9) Å] and O(5′1)—C(5′1) [1·180 (11) Å]. We have noticed in this laboratory

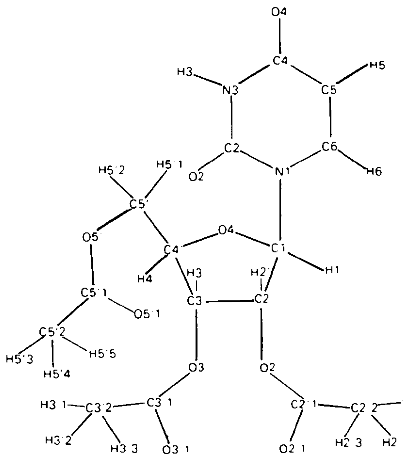

Fig. 1. Atomic numbering.

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* Lists of structure amplitudes, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39233 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* ($\text{Å}^2 \times 10^3$) *for non*-H *atoms with e.s.d.'s in parentheses*

$$U_{\text{eq}} = \tfrac{1}{3}\textstyle\sum_{i}\sum_{j} U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j .$$

	x	y	z	U_{eq}
N(1)	3499 (6)	−954 (3)	−1943 (3)	31 (1)
C(2)	2036 (8)	−1170 (4)	−1452 (3)	29 (1)
O(2)	535 (5)	−949 (3)	−1615 (2)	42 (1)
N(3)	2474 (6)	−1670 (3)	−758 (3)	33 (1)
C(4)	4113 (7)	−1998 (4)	−528 (3)	32 (1)
O(4)	4268 (5)	−2478 (3)	82 (3)	46 (1)
C(5)	5558 (7)	−1730 (4)	−1058 (3)	35 (1)
C(6)	5206 (8)	−1225 (4)	−1729 (3)	33 (1)
C(1′)	3260 (7)	−401 (4)	−2685 (3)	32 (1)
C(2′)	1722 (7)	−693 (4)	−3249 (3)	31 (1)
O(2′)	2513 (5)	−764 (3)	−4050 (2)	37 (1)
C(2′1)	1653 (10)	−1295 (5)	−4608 (4)	45 (2)
O(2′1)	311 (7)	−1701 (4)	−4465 (3)	69 (1)
C(2′2)	2664 (10)	−1324 (7)	−5401 (4)	71 (3)
C(3′)	491 (7)	163 (4)	−3202 (3)	30 (1)
O(3′)	−514 (5)	324 (3)	−3928 (2)	36 (1)
C(3′1)	−2169 (8)	−54 (5)	−3929 (4)	45 (2)
O(3′1)	−2717 (6)	−518 (4)	−3384 (3)	71 (2)
C(3′2)	−3185 (10)	247 (6)	−4669 (4)	69 (2)
C(4′)	1781 (8)	955 (4)	−3043 (3)	39 (1)
C(5′)	1016 (10)	1847 (4)	−2713 (5)	53 (2)
O(5′)	−198 (6)	1653 (3)	−2042 (3)	53 (1)
C(5′1)	−1953 (11)	1698 (5)	−2196 (5)	61 (2)
O(5′1)	−2544 (8)	1891 (5)	−2842 (4)	104 (2)
C(5′2)	−3049 (14)	1436 (8)	−1467 (6)	97 (3)
O(4′)	2964 (6)	551 (3)	−2456 (2)	41 (1)

Table 2. *Interatomic distances* (Å) *and angles* (°)

C(2)—N(1)	1·394 (7)	O(2′1)—C(2′1)	1·184 (9)
C(6)—N(1)	1·382 (7)	C(2′2)—C(2′1)	1·505 (9)
C(1′)—N(1)	1·463 (7)	O(3′)—C(3′)	1·425 (6)
O(2)—C(2)	1·199 (7)	C(4′)—C(3′)	1·513 (8)
N(3)—C(2)	1·382 (7)	C(3′1)—O(3′)	1·354 (7)
C(4)—N(3)	1·368 (7)	O(3′1)—C(3′1)	1·185 (9)
O(4)—C(4)	1·219 (7)	C(3′2)—C(3′1)	1·495 (10)
C(5)—C(4)	1·439 (8)	C(5′)—C(4′)	1·501 (9)
C(6)—C(5)	1·344 (8)	O(4′)—C(4′)	1·430 (7)
C(2′)—C(1′)	1·536 (7)	O(5′)—C(5′)	1·453 (9)
O(4′)—C(1′)	1·432 (7)	C(5′1)—O(5′)	1·340 (10)
O(2′)—C(2′)	1·443 (6)	O(5′1)—C(5′1)	1·180 (11)
C(3′)—C(2′)	1·537 (8)	C(5′2)—C(5′1)	1·498 (13)
C(2′1)—O(2′)	1·352 (7)		

C(6)—N(1)—C(2)	121·3 (4)	O(2′1)—C(2′1)—O(2′)	123·2 (6)
C(1′)—N(1)—C(2)	120·3 (4)	C(2′2)—C(2′1)—O(2′)	111·0 (6)
C(1′)—N(1)—C(6)	118·4 (4)	C(2′2)—C(2′1)—O(2′1)	125·7 (6)
O(2)—C(2)—N(1)	123·4 (5)	O(3′)—C(3′)—C(2′)	113·9 (4)
N(3)—C(2)—N(1)	113·7 (5)	C(4′)—C(3′)—C(2′)	102·9 (4)
N(3)—C(2)—O(2)	122·9 (5)	C(4′)—C(3′)—O(3′)	111·1 (4)
C(4)—N(3)—C(2)	128·1 (5)	C(3′1)—O(3′)—C(3′)	114·8 (4)
O(4)—C(4)—N(3)	120·3 (5)	O(3′1)—C(3′1)—O(3′)	122·7 (6)
C(5)—C(4)—N(3)	114·7 (5)	C(3′2)—C(3′1)—O(3′)	110·6 (6)
C(5)—C(4)—O(4)	125·0 (5)	C(3′2)—C(3′1)—O(3′1)	126·6 (6)
C(6)—C(5)—C(4)	119·3 (5)	C(5′)—C(4′)—C(3′)	117·2 (5)
C(5)—C(6)—N(1)	122·7 (5)	O(4′)—C(4′)—C(3′)	102·0 (4)
C(2′)—C(1′)—N(1)	116·3 (4)	O(4′)—C(4′)—C(5′)	109·8 (5)
O(4′)—C(1′)—N(1)	108·5 (4)	O(5′)—C(5′)—C(4′)	110·4 (5)
O(4′)—C(1′)—C(2′)	107·5 (4)	C(5′1)—O(5′)—C(5′)	117·5 (6)
O(2′)—C(2′)—C(1′)	104·9 (4)	O(5′1)—C(5′1)—O(5′)	123·2 (8)
C(3′)—C(2′)—C(1′)	101·7 (4)	C(5′2)—C(5′1)—O(5′)	112·1 (7)
C(3′)—C(2′)—O(2′)	110·3 (4)	C(5′2)—C(5′1)—O(5′1)	124·7 (8)
C(2′1)—O(2′)—C(2′)	117·2 (4)	C(4′)—O(4′)—C(1′)	107·8 (4)

(Low, 1983; Wilson, Low & Young, 1983) that carboxyl bonds are frequently less than expected for a conjugated C=O bond (1·21 Å). Values as low as 1·14 Å have been found in 3′,5′-di-*O*-acetyl-2′-deoxy-5-iodouridine (AIDU) (Wilson *et al.*, 1983). In 3′,5′-di-*O*-acetyluridine (de Graaff, Admiraal, Koen & Romers, 1977), a short acetyl C=O bond of 1·17 Å was corrected to 1·21 Å by allowing the O atoms to be disordered, although this prejudiced the planarity of the acetyl group. In the present molecule only one of the O atoms involved, O(5′1), has a slightly high temperature factor, the others being quite normal. There is thus no justification to assume disorder in this case. In the cases cited, there was no systematic lengthening or shortening of the ester O—C bond from its average value of 1·36 Å. Nor, in the case of ring carboxyls showing this bond shortening, were ring parameters unusual.

Conformational features. The conformation about the glycosyl bond is *syn*, with χ_{CN}[C(2)—N(1)—C(1′)—O(4′)] = 74·2 (6)°. The sugar pucker is $^3T_4$ [C(3′)-*endo*/C(4′)-*exo*], with pseudorotation angle P = 46·5 (6)° and degree of pucker $-\psi_{\text{m}} = 42{\cdot}4°$. This conformation, unusual for a pyrimidine nucleoside, has been previously found in 3′,5′-di-*O*-acetyl-2′-deoxy-2′-fluorouridine (DAF) (Suck, Saenger, Main, Germain & Declercq, 1974). The C(4′)—C(5′) conformation here is g^+ (*gauche–gauche*), whereas in DAF it is g^- (*trans–gauche*).

Hydrogen bonding and molecular stacking. There is one intermolecular hydrogen bond N(3)—H(3)···O(4)($-0{\cdot}5 + x$, $-0{\cdot}5 - y$, $-z$) of 2·913 (8) Å, the H(3)···O(4) distance being 1·99 Å. As was observed in AIDU (Wilson *et al.*, 1983), there is no base–base stacking present, the main stacking interaction again being a close contact of O(5′1) to a neighbouring base ring, of 2·90 (3) Å, as shown in Fig. 2. The pyrimidine base ring is essentially planar [maximum deviation of atom from plane: C(4) −0·02 (3) Å], as are the acetyl groups (all to within 0·02 Å).

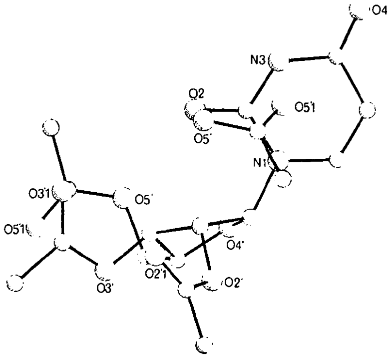

Fig. 2. View perpendicular to the pyrimidine ring, showing stacking of O(5′1). Only 5′-acetyl atoms of the second molecule are shown, and H atoms are omitted for clarity.

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cis-2,3,4a*β*,8a*β*-Tetramethyl-4a,5,8,8a-tetrahydro-1,4-naphthoquinone (TTN), $C_{14}H_{18}O_2$, and *cis*-2,3,4a*β*,8a*β*-Tetramethyl-4a,5,6,7,8,8a-hexahydro-1,4-naphthoquinone (THN), $C_{14}H_{20}O_2$

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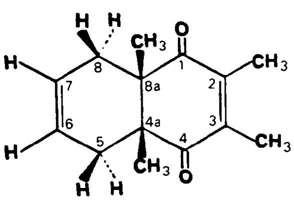
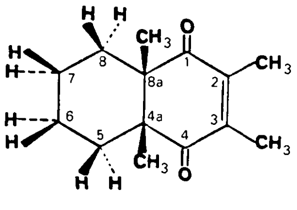
Abstract. TTN, THN: $M_r = 218{\cdot}30$, $220{\cdot}31$, orthorhombic, *Pbca*, $a = 26{\cdot}255$ (2), $26{\cdot}699$ (4), $b = 10{\cdot}387$ (1), $10{\cdot}413$ (1), $c = 8{\cdot}966$ (1), $9{\cdot}003$ (1) Å, $V = 2445{\cdot}2$ (5), $2502{\cdot}9$ (5) Å^3, $Z = 8$, $D_x = 1{\cdot}186$, $1{\cdot}169$ g cm^{-3}, $T = 295$ K, Mo $K\alpha$, $\lambda(K\alpha_1) = 0{\cdot}70930$ Å, $\mu = 0{\cdot}764$, $0{\cdot}761$ cm^{-1}, $F(000) = 944$, 960, final $R = 0{\cdot}081$, $0{\cdot}073$, for 1905, 939 observed reflections, respectively. The crystals are isostructural. In both structures the cyclohexene (TTN) and cyclohexane (THN) moieties are *cis*-fused to a half-chair cyclohex-2-ene-1,4-dione ring. In the TTN molecule the cyclohexene ring exists in a half-chair conformation, in the THN molecule the cyclohexane ring adopts a chair conformation.

Introduction. The similarity between the solid-state ^{13}C NMR spectra of TTN (I) and THN (II) (J. R. Scheffer & Y. F. Wong, private communication) suggests that these two molecules crystallize in isostructural lattices. The present crystallographic study was undertaken to establish their crystal structures and to determine the similarity between their molecular conformations.



(I)



(II)

Experimental. TTN and THN crystals from ethanol. D_m not determined. TTN m.p. 317–320 K, $0{\cdot}5 \times 0{\cdot}5 \times 0{\cdot}3$ mm; THN m.p. 315–317 K, $0{\cdot}2 \times 0{\cdot}2 \times 0{\cdot}5$ mm (mounted in a capillary tube because of air sensitivity). CAD-4 diffractometer, graphite-monochromatized Mo $K\alpha$ radiation. Lattice parameters from setting of 25 reflections with $15 \leq \theta \leq 22°$. 3054 unique reflections with $\theta \leq 27°$ for TTN, 2552 with $\theta \leq 25°$ for THN. ω–2θ scan for TTN, ω–$5/3\theta$ for THN, ω scan width $(0{\cdot}6 + 0{\cdot}3\tan\theta)°$ for TTN, $(0{\cdot}8 + 0{\cdot}3\tan\theta)°$ for THN, extended 25% on each side for background measurement, horizontal aperture $(1{\cdot}0 + \tan\theta)$mm, vertical aperture 4 mm. Lp corrections, no absorption corrections. Three standard reflections, 10% decay for TTN, stable for THN. Structures solved by direct methods using *SHELX* (Sheldrick, 1976) and refined by full-matrix least-squares minimizing $\sum w(|F_o| - |F_c|)^2$, 217 parameters consisting of 102 positional parameters, 96 anisotropic temperature factors, 18 isotropic temperature factors and a scale factor for TTN; 165 parameters consisting of 60 positional parameters, 96 anisotropic temperature factors, 8 isotropic temperature factors and a scale factor for THN. H atoms from a difference synthesis for TTN, but calculated for THN. Final $R = 0{\cdot}081$, $R_w = 0{\cdot}090$ for 1905 reflections for TTN, final R

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