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Structure of 5'-Acetylthymidine

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Abstract. $C_{12}H_{16}N_2O_6$, $M_r = 284.3$, orthorhombic, $P2_12_12_1$, $a = 9.262$ (1), $b = 30.658$ (2), $c = 4.788$ (1) Å, $V = 1359.5$ (2) Å^3, $Z = 4$, $D_x = 1.389$ Mg m^{-3}, Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å, $\mu = 0.97$ mm^{-1}, $F(000) = 600$, room temperature, $R = 0.034$ for 1490 observed reflections. The molecule has a C(2')-*endo* furanose ring associated with the base in the *anti* conformation. Atomic coordinates are presented for a standard thymine residue, which was derived from the bond distances and angles averaged over 21 structures retrieved from the Cambridge Crystallographic Database.

Introduction. Raman spectroscopic examination of the crystals of nucleosides and nucleotides whose structures are known from X-ray analysis has revealed several correlations between structure and spectrum, which have, in turn, been used for diagnosing the conformation of nucleic acids (Nishimura, Tsuboi, Sato & Aoki, 1986; Katahira, Nishimura, Tsuboi, Sato, Mitsui & Iitaka, 1986). The present study was undertaken as part of such investigations.

Experimental. Crystals grown from aqueous solution by slow evaporation, colorless plate, D_m not measured. Crystal dimensions: $0.10 \times 0.15 \times 0.30$ mm, Rigaku AFC-5 diffractometer, graphite-monochromated Cu $K\alpha$ radiation. Lattice parameters from 24 reflections $(56 < 2\theta < 81°)$. $\omega/2\theta$ scan, $2\theta \leq 140°$, $0 \leq h \leq 11$, $0 \leq k \leq 38$, $0 \leq l \leq 5$, three standard reflections: no variation. 1606 independent reflections measured, 1490 with $I \geq 2\sigma(I)$ considered observed. No absorption correction. Structure solved by direct methods, H atoms located from a difference Fourier map and their positions and isotropic thermal parameters refined. Full-matrix least-squares refinement,

anisotropic thermal parameters for non-H atoms, isotropic type I extinction correction (Becker & Coppens, 1974) with $g = 0.24$ (1) $\times 10^{-4}$, $\sum w(\Delta F)^2$ minimized, $w = 1$, $R = 0.034$, $wR = 0.033$, final $|\text{shift}/\sigma|_{\max} < 0.1$, $-0.16 \leq \Delta\rho \leq 0.14$ e Å^{-3}. The final atomic parameters are given in Table 1.* Bond distances and angles are listed in Table 2. All crystallographic calculations were performed on a VAX11/780 computer using the program system *XTAL*2.2 (Hall & Stewart, 1987) with the scattering factors as included in the program.

Discussion. A perspective view of the molecule is shown in Fig. 1. The conformation of the nucleoside moiety is quite normal. The pseudorotation coordinates (Sato, 1983) of the furanose ring are $\Pi = 37.8$ (3)° and $\Phi = 257.4$ (4)° and, therefore, the ring is puckered in a C(2')-*endo* form. The conformations about the C(1')—N(1) and the C(4')—C(5') bonds are *anti* and *trans–gauche,* the torsion angles O(4')—C(1')—N(1)—C(6), C(2')—C(1')—N(1)—C(6) and C(3')—C(4')—C(5')—O(5') being 48.5 (3), 103.4 (3) -174.3 (2)°, respectively.

To see whether the molecular dimensions of the base are normal or not, crystal structures containing the unsubstituted thymine residue were retrieved from the Cambridge Crystallographic Database (Allen *et al.,* 1979) and the bond distances and angles were averaged over 21 accurate structures* using the program *GEOM*

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* Lists of H-atom parameters, anisotropic thermal parameters, structure factors and reference codes for the crystal structures used in the analysis of the thymine residue have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44610 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å² × 10³)

$$U_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
N(1)	0·4933 (2)	0·42254 (6)	0·3597 (5)	29·9 (6)
C(2)	0·6011 (2)	0·45293 (8)	0·3904 (6)	29·8 (7)
N(3)	0·7165 (2)	0·44697 (7)	0·2128 (5)	34·6 (7)
C(4)	0·7355 (3)	0·41365 (8)	0·0231 (6)	34·7 (8)
C(5)	0·6228 (3)	0·38135 (8)	0·0162 (6)	33·0 (7)
C(6)	0·5063 (3)	0·38802 (8)	0·1769 (6)	33·2 (8)
O(2)	0·5953 (2)	0·48277 (6)	0·5593 (4)	37·9 (6)
O(4)	0·8447 (2)	0·41264 (7)	−0·1237 (5)	52·5 (7)
C(7)	0·6390 (4)	0·3425 (1)	−0·1734 (8)	50 (1)
O(4')	0·3020 (2)	0·39084 (5)	0·6147 (4)	33·5 (5)
C(1')	0·3539 (2)	0·43073 (8)	0·4996 (6)	29·4 (7)
C(2')	0·2384 (3)	0·44614 (9)	0·2999 (6)	34·7 (8)
C(3')	0·1014 (3)	0·43208 (9)	0·4460 (7)	35·3 (8)
C(4')	0·1470 (3)	0·38881 (9)	0·5786 (6)	35·9 (8)
O(3')	0·0682 (2)	0·46392 (7)	0·6496 (5)	47·6 (7)
C(5')	0·1081 (4)	0·3496 (1)	0·405 (1)	58 (1)
O(5')	0·1412 (3)	0·31001 (7)	0·5546 (6)	70·1 (9)
C(6')	0·2543 (5)	0·2866 (1)	0·4699 (9)	70 (1)
O(6')	0·3303 (4)	0·29645 (9)	0·2769 (8)	96 (1)
C(7')	0·275 (1)	0·2473 (1)	0·651 (1)	107 (3)

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

N(1)—C(2)	1·373 (3)	N(1)—C(6)	1·379 (3)
N(1)—C(1')	1·477 (3)	C(2)—N(3)	1·378 (3)
C(2)—O(2)	1·222 (3)	N(3)—C(4)	1·378 (4)
C(4)—C(5)	1·439 (3)	C(4)—O(4)	1·232 (3)
C(5)—C(6)	1·341 (4)	C(5)—C(7)	1·504 (4)
O(4')—C(1')	1·425 (3)	O(4')—C(4')	1·447 (3)
C(1')—C(2')	1·510 (4)	C(2')—C(3')	1·511 (4)
C(3')—C(4')	1·530 (4)	C(3')—O(3')	1·413 (4)
C(4')—C(5')	1·505 (5)	C(5')—O(5')	1·444 (4)
O(5')—C(6')	1·333 (5)	C(6')—O(6')	1·200 (6)
C(6')—C(7')	1·497 (7)		

C(2)—N(1)—C(6)	121·7 (2)	C(2)—N(1)—C(1')	118·2 (2)
C(6)—N(1)—C(1')	119·6 (2)	N(1)—C(2)—N(3)	114·1 (2)
N(1)—C(2)—O(2)	123·1 (2)	N(3)—C(2)—O(2)	122·8 (2)
C(2)—N(3)—C(4)	127·1 (2)	N(3)—C(4)—C(5)	115·7 (2)
N(3)—C(4)—O(4)	119·9 (2)	C(5)—C(4)—O(4)	124·4 (3)
C(4)—C(5)—C(6)	117·7 (2)	C(4)—C(5)—C(7)	119·1 (2)
C(6)—C(5)—C(7)	123·2 (2)	N(1)—C(6)—C(5)	123·4 (2)
C(1')—O(4')—C(4')	109·0 (2)	N(1)—C(1')—O(4')	108·9 (2)
N(1)—C(1')—C(2')	112·7 (2)	O(4')—C(1')—C(2')	105·9 (2)
C(1')—C(2')—C(3')	102·2 (2)	C(2')—C(3')—C(4')	102·0 (2)
C(2')—C(3')—O(3')	107·8 (2)	C(4')—C(3')—O(3')	111·9 (3)
O(4')—C(4')—C(3')	106·6 (2)	O(4')—C(4')—C(5')	109·7 (2)
C(3')—C(4')—C(5')	113·4 (3)	C(4')—C(5')—O(5')	110·2 (3)
C(5')—O(5')—C(6')	117·9 (3)	O(5')—C(6')—O(6')	124·1 (4)
O(5')—C(6')—C(7')	111·1 (5)	O(6')—C(6')—C(7')	124·8 (5)

Table 3. *Mean bond distances* (Å) *and angles* (°) *of* 21 *thymine residues retrieved from the Cambridge Crystallographic Database* (*standard deviations in parentheses*)

N(1)—C(2)	1·377 (7)	N(1)—C(6)	1·379 (8)
N(1)—C(1')	1·469 (9)	C(2)—N(3)	1·375 (5)
C(2)—O(2)	1·217 (9)	N(3)—C(4)	1·381 (7)
C(4)—C(5)	1·440 (9)	C(4)—O(4)	1·232 (7)
C(5)—C(6)	1·340 (8)	C(5)—C(7)	1·500 (7)

C(2)—N(1)—C(6)	121·2 (5)	C(2)—N(1)—C(1')	118·3 (10)
C(6)—N(1)—C(1')	120·4 (9)	N(1)—C(2)—N(3)	114·7 (6)
N(1)—C(2)—O(2)	123·3 (6)	N(3)—C(2)—O(2)	122·0 (8)
C(2)—N(3)—C(4)	126·8 (5)	N(3)—C(4)—C(5)	115·6 (5)
N(3)—C(4)—O(4)	119·9 (6)	C(5)—C(4)—O(4)	124·5 (7)
C(4)—C(5)—C(6)	118·1 (6)	C(4)—C(5)—C(7)	118·9 (6)
C(6)—C(5)—C(7)	123·0 (5)	N(1)—C(6)—C(5)	123·5 (6)

Table 4. *Cartesian coordinates for a standard thymine residue* (Å)

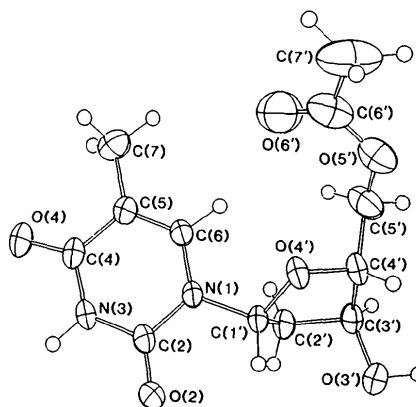|	x	y	z
N(1)	0·0000	0·0000	0·0000
C(2)	−1·2001	0·6754	0·0000
N(3)	−1·0894	2·0459	0·0000
C(4)	0·0796	2·7808	0·0000
C(5)	1·2977	2·0130	0·0000
C(6)	1·2019	0·6764	0·0000
O(2)	−2·2811	0·1163	0·0000
O(4)	0·0310	4·0119	0·0000
C(7)	2·6110	2·7377	0·0000
H(N3)	−1·9831	2·5740	0·0000
H(C6)	2·0927	0·0570	0·0000
H1(C7)	2·7089	3·3426	0·8353
H2(C7)	3·4080	2·0758	0·0000
H3(C7)	2·7089	3·3426	−0·8353
C(1')	−0·0269	−1·4688	0·0000

Fig. 1. A perspective view of the molecule with atom-numbering scheme, prepared with *ORTEP* in *XTAL*2.2 (Hall & Stewart, 1987).
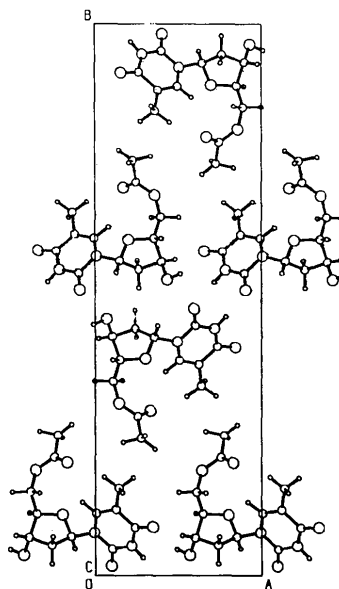

Fig. 2. A [001] projection of the unit cell, prepared with *PLUTO* (Motherwell & Clegg, 1978).

(Motherwell, 1978). Compared with the mean values (Table 3), those observed here are normal. We applied the procedure described by Taylor & Kennard (1982), to calculate a standard geometry for the thymine residue (Table 4). Here a standard geometry is defined as one whose bond distances and angles are as close as possible to the average ones observed in crystal structures. Also included in the list are the H atoms, which were calculated with the data from two neutron structures. The use of such standard atomic co-ordinates has many applications in structural studies of nucleic acids and those for the other bases have already been compiled (Taylor & Kennard, 1982).

Two available protons in the molecule are both involved in intermolecular hydrogen bonds, i.e. N(3)—H···O(2) [2·867 (3) Å] and O(3')—H···O(4) [2·817 (3) Å]. The packing scheme in the crystal is shown in Fig. 2.

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Structure of 6-Dodecyl-2-methoxy-1,4-benzoquinone, a New Synthetic Contact Allergen

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Abstract. $C_{19}H_{30}O_3$, $M_r = 306·45$, triclinic, $P\bar{1}$, $a = 5·453$ (1), $b = 5·608$ (1), $c = 30·129$ (2) Å, $\alpha = 85·85$ (1), $\beta = 88·66$ (1), $\gamma = 83·02$ (1)°, $V = 912·0$ (1) Å^3, $Z = 2$, $D_x = 1·116$ Mg m^{-3}, Cu $K\alpha$ radiation, $\lambda = 1·5418$ Å, $\mu = 0·548$ mm^{-1}, $F(000) = 336$, $T = 296$ K, R is 0·040 for 2489 observed unique reflections. The aliphatic side chain is slightly rotated from the quinone ring. The angle between the quinone-ring plane and the mean dodecyl-chain plane is 20·8 (2)°. The average C_{sp^3}—C_{sp^3} bond lengths and corresponding angles of the side chain are 1·515 (5) Å and 113·8 (3)°. The average dimensions of the quinone ring are C—C 1·477 (4), C=C 1·337 (4), C=O 1·222 (3) Å, C—C—C 118·9 (3), C=C—C 120·6 (3), O=C—C 120·6 (3)°. Neighbouring molecules form dimers by C—H···O interactions across centres of symmetry [C(3)···O(3) 3·413 (2) Å]. The dimers are linked together via methyl H and carbonyl O along [100] [C(19)···O(3) 3·338 (3) Å]; O(3) is a bifurcated acceptor.