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# Structure of 1-Acetylthymine

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**Abstract.** $C_7H_8N_2O_3$, $M_r = 168.50$, monoclinic, $P2_1/n$, $a = 5.074\,(3)$, $b = 8.611\,(3)$, $c = 17.476\,(4)$ Å, $\beta = 94.57\,(4)^\circ$, $V = 761.2\,(5)$ Å$^3$, $Z = 4$, $D_x = 1.467$ g cm$^{-3}$, $\lambda(\text{Cu } K\alpha) = 1.54178$ Å, $\mu = 9.5$ cm$^{-1}$, $F(000) = 352$, $T = 294$ K, $R = 0.038$ for 833 observed reflections. With respect to other thymine derivatives substituted at N(1), N(1)—C(2) and N(1)—C(6) bond distances in the title compound are thc longest reported to date, while the C(5)—C(6) bond distance is the shortest observed so far. An intramolecular hydrogen bond between H(6) and O(1) is revealed from the structure analysis. Intermolecular hydrogen bonds are inferred from the structure with H(6)($x$, $y$, $z$) of one molecule interacting with O(1)($1 - x$, $1 - y$, $1 - z$) of the other. This system appears to be the first reported example in which an H atom bonded to C participates in a bifurcated hydrogen bond. An additional intermolecular hydrogen bond is observed between O(4)($x$, $y$, $z$) and H(3)($-x - 1$, $-y$, $1 - z$). The title compound packs as a series of parallel planar $\pi$-stacked ribbons of molecules, with adjacent ribbons separated by approximately 3.2 Å.

**Introduction.** Within our program of study on modified nucleosides, we have synthesized the title compound as a precursor to the synthesis of a strategically altered nucleoside. The present structural study was undertaken to examine the effects of the electron-withdrawing acetyl substituent at N(1) on the structure of the pyrimidine ring, and as a basis for comparison with our future compounds incorporating this molecule as a fragment.

**Experimental.** The title compound was synthesized using the method of Spector & Keller (1958). Data were collected using a colorless crystal of dimensions 0.30 × 0.45 × 0.40 mm on a Rigaku AFC6S diffractometer equipped with an evacuated beam collimator and detector tunnel. Graphite-monochromated Cu $K\alpha$ radiation was employed with the intensities measured 400 mm from the crystal. Measured data to $2\theta = 110^\circ$ included reflections $h$ 0–5, $k$ 0–9, $l$ −18–18. Scans were of the $\omega$–$2\theta$ type, where the $\omega$-scan speed was 32° min$^{-1}$. The scan width in $\omega$ was $(1.68 + 0.30\tan\theta)^\circ$ and weak reflections were rescanned up to eight times and the counts accumulated. Of the 1185 reflections measured, 1047 were considered unique; for averaged data, $R_{\text{int}} = 0.022$. 839 reflections were classified as observed having $F^2 \geq 3\sigma(F^2)$. Three standard reflections monitored throughout data collection showed less than 1% change in their intensities over the period of the experiment indicating no decay correction was required. Lorentz–polarization corrections were applied and an empirical absorption correction was included in the data-processing step (transmission factors, 0.95–1.00, based on $\psi$ scans of three reflections). Six reflections (120, 12$\bar{1}$, 200, 020, 101 and 002) had intensities that far exceeded the linear range of the detector and were flagged so as not to be used in structure solution and refinement.

The structure was solved by direct methods and refined using programs in the *TEXSAN* (Molecular Structure Corporation, 1985) software package. The structure was refined on $F$, initially with non-H atoms only. H-atom positions were subsequently determined from difference Fourier maps and included for the remaining cycles of refinement. Using all of the observed data, convergence was reached at $R = 0.038$ and $wR = 0.055$. For all data, $R = 0.044$ and $wR = 0.056$. The function minimized throughout refinement was $\sum w\Delta^2$ ($\Delta = |F_o| - |F_c|$),

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where $w = \sigma^{-2}(F_o)$; $S = 2.54$ and the maximum $\Delta/\sigma = 0.005$ on the final cycle. The final difference Fourier map showed random fluctuations of $\pm 0.1$ e Å$^{-3}$. Scattering factors for all non-H atoms were from Cromer & Waber (1974) and from Stewart, Davidson & Simpson (1965) for H atoms. Final atomic positional parameters and equivalent isotropic thermal parameters are given in Table 1.* Fig. 1 shows the molecule in the asymmetric unit with atom labels.

**Discussion.** The bond distances and angles (Table 2) in the C(2)—N(3)—C(4)—C(5) portion of the thymine moiety agree well with those found in 1-methylthymine (Hoogsteen, 1963), thymidine (Young, Tollin & Wilson, 1969), 1-(2-hydroxyethyl)-thymine monohydrate (Shibata, Takenaka, Sasada & Ohki, 1985) and 1-(2-carbamoylethyl)thymine (Kizawa, Takenaka & Sasada, 1988). However, in the remaining fragment of the thymine moiety, the title compound exhibits significant structural differences when compared to all previously determined structures of thymine derivatives with substituents at N(1). Notably, the bond lengths N(1)—C(2), 1.400 (3) Å, and N(1)—C(6), 1.404 (3) Å, in the title compound are the longest reported to date, whereas the C(5)—C(6) bond length of 1.322 (3) Å is the shortest bond observed between these two C atoms. In all other thymine derivatives substituted at N(1) whose crystal structures have been determined to date [based on a search of the Cambridge Structural Database (Allen, Bellard, Brice, Cartwright, Doubleday, Higgs, Hummelink, Hummelink-Peters, Kennard, Motherwell, Rodgers & Watson, 1979)], the bond lengths N(1)—C(2), N(1)—C(6) and C(5)—C(6) lie within the ranges 1.35–1.39, 1.36–1.38 and 1.33–1.35 Å, respectively. As the above bond distances indicate, the N(1)—C bonds in the title compound possess a significantly lower bond order than that found in other N(1)-substituted thymine derivatives, while the C(5)—C(6) bond possesses a bond order that is slightly higher. This suggests that the lone pair of electrons on N(1) does not readily delocalize into the pyrimidine ring, hence locking the resonance form of the C(2)—N(1)—C(6)—C(5) bonding framework into that shown below. The bond length N(1)—C(8), 1.447 (3) Å, which is only slightly shorter than the average length of a planar C$sp^3$—N$sp^2$ bond (1.465 Å; Allen, Kennard, Watson, Brammer, Orpen

Table 1. *Positional parameters and* $B_{eq}$ *values* ($B_{iso}$ *values for* H*'s*) *for* 1*-acetylthymine with e.s.d.'s in parentheses*

$$B_{eq} = (8\pi^2/3)\sum_{i=1}^{3}\sum_{j=1}^{3} U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

| | $x$ | $y$ | $z$ | $B_{eq}$ (Å$^2$) |
|---|---|---|---|---|
| O(1) | 0.3938 (4) | 0.4747 (2) | 0.3980 (1) | 6.6 (1) |
| O(2) | −0.2302 (3) | 0.1942 (2) | 0.3312 (1) | 6.5 (1) |
| O(4) | −0.2990 (3) | 0.0611 (2) | 0.57787 (9) | 5.39 (8) |
| N(1) | 0.0685 (3) | 0.3064 (2) | 0.4213 (1) | 4.32 (8) |
| N(3) | −0.2605 (4) | 0.1375 (2) | 0.4553 (1) | 4.8 (1) |
| C(2) | −0.1461 (4) | 0.2118 (3) | 0.3967 (1) | 4.7 (1) |
| C(4) | −0.1833 (4) | 0.1407 (3) | 0.5325 (1) | 4.4 (1) |
| C(5) | 0.0407 (4) | 0.2395 (2) | 0.5547 (1) | 4.3 (1) |
| C(6) | 0.1527 (4) | 0.3143 (2) | 0.4997 (1) | 4.4 (1) |
| C(7) | 0.1380 (6) | 0.2463 (4) | 0.6373 (1) | 5.5 (1) |
| C(8) | 0.2188 (5) | 0.3951 (3) | 0.3700 (1) | 4.9 (1) |
| C(9) | 0.1536 (7) | 0.3860 (4) | 0.2861 (2) | 6.5 (2) |
| H(3) | −0.384 (5) | 0.076 (3) | 0.443 (1) | 5.7 (6) |
| H(6) | 0.296 (4) | 0.381 (2) | 0.508 (1) | 4.2 (4) |
| H(7*A*) | 0.196 (4) | 0.144 (3) | 0.657 (1) | 6.1 (6) |
| H(7*B*) | −0.019 (6) | 0.274 (3) | 0.673 (2) | 8.4 (7) |
| H(7*C*) | 0.280 (5) | 0.311 (3) | 0.645 (1) | 6.3 (6) |
| H(9*A*) | −0.036 (6) | 0.418 (2) | 0.275 (2) | 7.6 (7) |
| H(9*B*) | 0.147 (5) | 0.280 (4) | 0.267 (2) | 8.2 (8) |
| H(9*C*) | 0.291 (5) | 0.458 (3) | 0.265 (2) | 7.7 (7) |

Table 2. *Intramolecular bond distances* (Å) *and angles* (°) *involving non-*H *atoms with e.s.d.'s in parentheses*

| | | | |
|---|---|---|---|
| O(1)—C(8) | 1.195 (3) | N(3)—C(2) | 1.375 (3) |
| O(2)—C(2) | 1.200 (3) | N(3)—C(4) | 1.375 (3) |
| O(4)—C(4) | 1.232 (3) | C(4)—C(5) | 1.447 (3) |
| N(1)—C(2) | 1.400 (3) | C(5)—C(6) | 1.322 (3) |
| N(1)—C(6) | 1.404 (3) | C(5)—C(7) | 1.490 (3) |
| N(1)—C(8) | 1.441 (3) | C(8)—C(9) | 1.480 (4) |

| | | | |
|---|---|---|---|
| C(2)—N(1)—C(6) | 119.8 (2) | N(3)—C(4)—C(5) | 115.5 (2) |
| C(2)—N(1)—C(8) | 123.7 (2) | C(4)—C(5)—C(6) | 117.8 (2) |
| C(6)—N(1)—C(8) | 116.5 (2) | C(4)—C(5)—C(7) | 118.3 (2) |
| C(2)—N(3)—C(4) | 128.1 (2) | C(6)—C(5)—C(7) | 123.8 (2) |
| O(2)—C(2)—N(1) | 125.1 (2) | N(1)—C(6)—C(5) | 124.8 (2) |
| O(2)—C(2)—N(3) | 120.9 (2) | O(1)—C(8)—N(1) | 117.6 (2) |
| N(1)—C(2)—N(3) | 114.0 (2) | O(1)—C(8)—C(9) | 122.4 (2) |
| O(4)—C(4)—N(3) | 120.5 (2) | N(1)—C(8)—C(9) | 120.1 (2) |
| O(4)—C(4)—C(5) | 124.0 (2) | | |

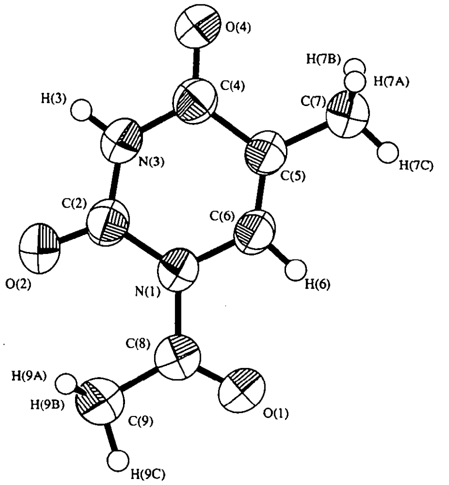

Fig. 1. An *ORTEP*II plot (Johnson, 1976) of 1-acetylthymine with ellipsoids at the 50% probability level.

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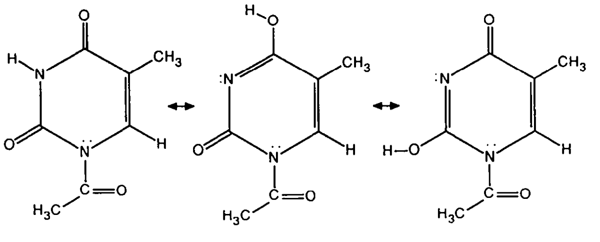
* Tables of anisotropic thermal parameters, bond distances and angles involving H atoms, and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54783 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: BR0006]

& Taylor, 1987), implies that the lone pair of electrons on N(1) does not tend to delocalize into the exocyclic acetyl substituent to any significant extent.



The title compound is planar within ±0.0245 Å, while the pyrimidine ring alone is planar within ±0.0155 Å. The planar configuration of the molecule places O(1) and H(6) 2.18 (2) Å apart, approximately 0.5 Å closer together than the sum of their van der Waals radii (Bondi, 1964). The proximity of O(1) and H(6), coupled with the concommitant closing of the bond angles O(1)—C(8)—N(1) towards H(6) [117.6 (2) compared with 122.4 (2)° for O(1)—C(8)—C(9)] and N(1)—C(6)—H(6) towards O(1) [111 (1) compared with 124 (1)° for C(5)—C(6)—H(6)], suggests that O(1) and H(6) interact electrostatically in a hydrogen-bonding-like interaction. The C(6)—H(6)···O(1) angle is 108 (1)°, and is in accordance with the generally accepted criterion for hydrogen-bond geometries that the donor–proton···acceptor angle be greater than 90° (Taylor & Kennard, 1982). Hydrogen-bonding interactions between H atoms bonded to C and O have been observed in numerous other structures (Taylor & Kennard, 1982, and references therein).

Further to the presence of the non-classical C—H···O intramolecular hydrogen bond in the present structure, there is evidence of intermolecular C—H···O bonding, with H(6)(*x*, *y*, *z*) of one molecule forming a hydrogen bond with O(1)(1 − *x*, 1 − *y*, 1 − *z*) of the other. The contact distance O(1)···H(6) is 2.51 (2) Å, which is approximately 0.2 Å less than the sum of the van der Waals radii of O and H (Bondi, 1964). The angle C(6)—H(6)···O(1) is 148 (1)°. It is interesting to note that this appears to be the first reported structure in which an H atom bonded to C is found participating in a bifurcated hydrogen bond. Another hydrogen bond inferred from this structure and observed in at least one other thymine derivative (Kizawa *et al.*, 1988) is O(4)(*x*, *y*, *z*) to H(3)(−*x* − 1, −*y*, 1 − *z*). The contact distance O(4)···H(3) is 2.00 (2) Å and the angle N(3)—H(3)···O(4) is 174 (2)°. It is apparent from Fig. 2 that the crystal packing is influenced by such intermolecular interactions. The hydrogen bonds present stitch together molecules of the title compound into a series of ribbons, planar to within ±0.249 Å, separated by approximately 3.2 Å. Molecules in adjacent ribbons participate in $\pi$–$\pi$ stacking interactions, as O(1)(*x*, *y*, *z*) overlaps C(2)(1 + *x*, *y*, *z*), with an interatomic separation of 3.254 (4) Å.

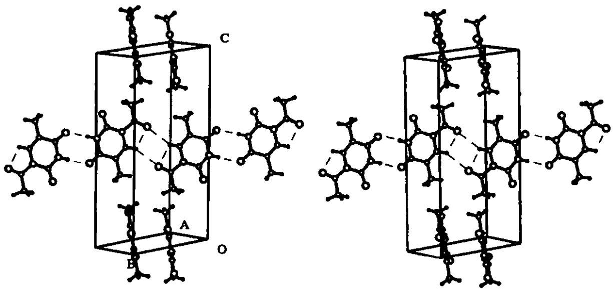


Fig. 2. A *PLUTO* (Motherwell & Clegg, 1978) stereopacking diagram of the title structure. Hydrogen bonds are shown as dashed lines.

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