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Structure and Conformation of 5-Hydroxymethyl-2′-deoxycytidine, $C_{10}H_{15}N_3O_5$

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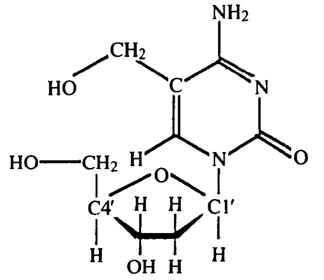
Abstract

The deoxyribose ring in the title compound adopts a C(3′)-*endo* envelope conformation (^3E), with the glycosyl linkage *anti* [χ = 195.8 (1)°]. The pseudorotational parameters are P = 10.2 (2)° and τ_m = 32.1 (2)°. The exocyclic side chain at C(5′) has the *t* conformation [γ = 174.6 (2)°]. The hydroxymethyl group side chain at C(5) is on the opposite side of the pyrimidine plane as is O(4′) of the furanose ring.

Comment

Oxopyrimidines are novel constituents of the DNA of certain lytic bacteriophages (Kallen, Simon & Mamur, 1962; Roscoe & Tucker, 1964; Witmer & Wiatr, 1985). The title compound, 5-hydroxymethyl-2′-deoxycytidine (HMdCyd) (I), was synthesized and its molecular conformation was determined.



(I)

The bond lengths and angles for HMdCyd are in the range reported for 2′-deoxycytidine nucleosides (Young & Wilson, 1975; Kashino, Negishi & Hayatsu, 1988; Low, Tollin, Howie & Wilson, 1988; Silverton, Quinn, Haugwitz & Todaro, 1988; Jia, Tourigny, Stuart, Delbaere & Gupta, 1990*a*,*b*; De Winter, Blaton, Peeters, De Ranter, Van Aerschot & Herdewijn, 1991). The glycosidic bond has the *anti* conformation and the glycosidic torsion angle C(2)—N(1)—C(1′)—O(4′) is χ = 195.8 (1)°. The exocyclic 5′-CH_2OH side chain has the *t* conformation [γ = 174.6 (2)°]. Although, the g^+ conformation is the most common found in cytidine and deoxycytidine compounds, the *t* conformation has been reported for 5-methyl-2′-deoxycytidine (Sato, 1988) and 5-methoxymethyl-N^4-methyl-2′-deoxycytidine (Jia *et al.*, 1990*b*). The HMdCyd molecule adopts a C(3′)-*endo* envelope conformation. The displacement of the C(3′) atom from the mean plane through the other four ring atoms is 0.502 (3) Å in (I). The values calculated for the two pseudorotational parameters (Altona & Sundaralingam, 1972) of the furanose ring torsion angles are

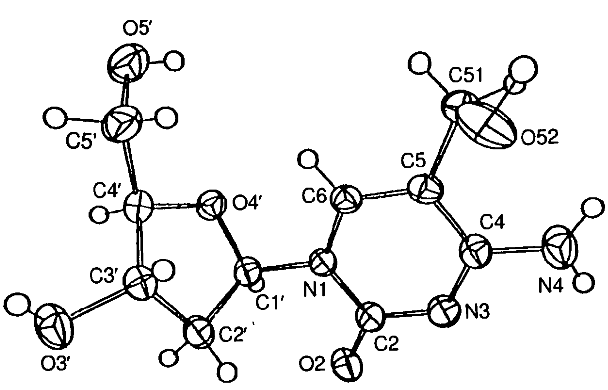


Fig. 1. A perspective view (*ORTEP*II; Johnson, 1976) of HMdCyd. Thermal ellipsoids are drawn at the 50% probability level.

the pseudorotational phase angle $P = 10.2\ (2)^\circ$ and puckering amplitude $\tau_m = 32.1\ (2)^\circ$. This result indicates that the deoxyribose moiety of (I) has a typical N conformation. The hydroxymethyl group at C(5) of the pyrimidine ring is on the opposite side of the pyrimidine plane as is the O(4′) of the furanose ring. The pyrimidine ring is planar, the largest deviation from the mean plane being 0.0189 (3) Å. There are several intermolecular hydrogen bonds which are summarized in Table 3.

Experimental

Crystal data

$C_{10}H_{15}N_3O_5$
$M_r = 257.3$
Monoclinic
$P2_1$
$a = 5.0110\ (4)$ Å
$b = 13.010\ (3)$ Å
$c = 8.922\ (1)$ Å
$\beta = 93.150\ (8)^\circ$
$V = 580.7\ (1)$ Å^3
$Z = 2$
$D_x = 1.471$ Mg m^{-3}
$D_m = 1.480$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 25 reflections
$\theta = 17.04$–38.30°
$\mu = 0.969$ mm^{-1}
$T = 287\ (1)$ K
Rod
0.925 × 0.20 × 0.15 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2548 measured reflections
1247 independent reflections
1247 observed reflections
$R_{\rm int} = 0.0133$

$\theta_{\rm max} = 75^\circ$
$h = -6 \rightarrow 6$
$k = 0 \rightarrow 16$
$l = -11 \rightarrow 11$
3 standard reflections
frequency: 83.33 min
intensity variation: none

Refinement

Refinement on F
$R = 0.030$
$wR = 0.036$
$S = 3.274$
1247 reflections
223 parameters
All H-atom parameters refined
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\rm max} = 0.0055$

$\Delta\rho_{\rm max} = 0.189$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.197$ e Å^{-3}
Extinction correction: Larson (1970)
Extinction coefficient: 7.03×10^{-5}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

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

	x	y	z	$U_{\rm eq}$
N(1)	0.0479 (3)	0.8350	0.7275 (1)	0.0267 (4)
C(2)	−0.1053 (4)	0.9231 (2)	0.7041 (2)	0.0295 (4)
O(2)	−0.0613 (3)	0.9968 (1)	0.7891 (1)	0.0405 (4)
N(3)	−0.2960 (3)	0.9240 (1)	0.5909 (2)	0.0335 (4)
C(4)	−0.3453 (4)	0.8400 (2)	0.5080 (2)	0.0302 (4)
N(4)	−0.5383 (4)	0.8458 (2)	0.3990 (2)	0.0457 (5)
C(5)	−0.1959 (3)	0.7477 (2)	0.5317 (2)	0.0279 (4)
C(51)	−0.2590 (4)	0.6497 (2)	0.4489 (2)	0.0328 (5)
O(52)	−0.4859 (4)	0.6053 (2)	0.5148 (2)	0.0451 (5)
C(6)	0.0012 (3)	0.7498 (2)	0.6417 (2)	0.0275 (4)
C(1′)	0.2616 (3)	0.8387 (2)	0.8510 (2)	0.0283 (4)
C(2′)	0.1485 (4)	0.8271 (2)	1.0054 (2)	0.0333 (5)
C(3′)	0.1826 (3)	0.7123 (2)	1.0384 (2)	0.0274 (4)
O(3′)	0.2085 (3)	0.6941 (1)	1.1947 (1)	0.0382 (4)
C(4′)	0.4343 (3)	0.6862 (2)	0.9579 (2)	0.0293 (4)
O(4′)	0.4393 (2)	0.7561 (1)	0.8323 (1)	0.0314 (3)
C(5′)	0.4408 (5)	0.5766 (2)	0.9000 (2)	0.0420 (6)
O(5′)	0.6643 (4)	0.5565 (2)	0.8140 (2)	0.0521 (5)

Table 2. *Selected geometric parameters* (Å, °)

N(1)—C(2)	1.388 (2)	C(51)—O(52)	1.430 (3)
N(1)—C(6)	1.360 (2)	C(1′)—C(2′)	1.526 (2)
N(1)—C(1′)	1.495 (2)	C(1′)—O(4′)	1.411 (2)
C(2)—O(2)	1.235 (2)	C(2′)—C(3′)	1.529 (3)
C(2)—N(3)	1.352 (2)	C(3′)—O(3′)	1.413 (2)
N(3)—C(4)	1.335 (3)	C(3′)—C(4′)	1.523 (2)
C(4)—N(4)	1.335 (3)	C(4′)—O(4′)	1.444 (2)
C(4)—C(5)	1.424 (3)	C(4′)—C(5′)	1.518 (3)
C(5)—C(51)	1.499 (3)	C(5′)—O(5′)	1.416 (3)
C(5)—C(6)	1.354 (2)		
C(2)—N(1)—C(6)	120.8 (1)	N(1)—C(6)—C(5)	121.3 (2)
C(2)—N(1)—C(1′)	116.9 (1)	N(1)—C(1′)—C(2′)	112.1 (1)
C(6)—N(1)—C(1′)	122.3 (1)	N(1)—C(1′)—O(4′)	108.7 (1)
N(1)—C(2)—O(2)	118.0 (2)	C(2′)—C(1′)—O(4′)	107.4 (1)
N(1)—C(2)—N(3)	118.8 (2)	C(1′)—C(2′)—C(3′)	103.1 (2)
O(2)—C(2)—N(3)	123.1 (2)	C(2′)—C(3′)—O(3′)	110.9 (2)
C(2)—N(3)—C(4)	120.6 (2)	C(2′)—C(3′)—C(4′)	102.3 (2)
N(3)—C(4)—N(4)	117.5 (2)	O(3′)—C(3′)—C(4′)	113.2 (1)
N(3)—C(4)—C(5)	121.9 (2)	C(3′)—C(4′)—O(4′)	106.0 (2)
N(4)—C(4)—C(5)	120.6 (2)	C(3′)—C(4′)—C(5′)	113.8 (2)
C(4)—C(5)—C(51)	123.3 (2)	O(4′)—C(4′)—C(5′)	109.0 (1)
C(4)—C(5)—C(6)	116.6 (2)	C(1′)—O(4′)—C(4′)	110.5 (1)
C(51)—C(5)—C(6)	120.0 (2)	C(4′)—C(5′)—O(5′)	113.0 (2)
C(5)—C(51)—O(52)	107.0 (2)		

Table 3. *Intermolecular hydrogen-bonding geometry* (Å)

D—H$\cdots A$	H$\cdots A$	$D\cdots A$
O(52)—H(52)$\cdots$N(3$^{\rm i}$)	1.91	2.74
O(3′)—H(32′)$\cdots$O(2$^{\rm ii}$)	1.91	2.68
N(4)—H(4′)$\cdots$O(3′$^{\rm iii}$)	2.08	2.93
O(5′)—H(52′)$\cdots$O(52$^{\rm iv}$)	2.06	2.81

Symmetry codes: (i) $-1 - x, y - \frac{1}{2}, 1 - z$; (ii) $-x, y - \frac{1}{2}, 2 - z$; (iii) $x - 1, y, z - 1$; (iv) $1 + x, y, z$.

A Bayesian treatment was applied to the data using *Xtal*3.0 (Hall & Stewart, 1990).

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: ST1089). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Ethoxycarbonylcholine Picrate Hemihydrate

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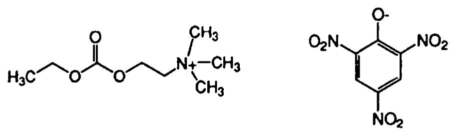
Abstract

The ethoxycarbonylcholine ion in the title compound ($C_8H_{18}NO_3^+.C_6H_2N_3O_7^-.0.5H_2O$) adopts a partly folded conformation with C—O—C—C and O—C—C—N torsion angles of ±174.59 (7) and ∓83.60 (9)°, respectively. The carbonyl C atom has a partial positive charge, and electrostatic interactions are observed between this C atom and the nitro groups of the picrate ion. Interactions between the quaternary ammonium group and the O atoms of the ester group may be described as (CH···O) hydrogen bonds. Each phenolate O atom is involved in a hydrogen bond with a water molecule, forming a picrate–water–picrate linkage. The water molecule is situated on a twofold axis.

Comment

Acetylcholine is a neurotransmitter in the cholinergic nervous system. Therefore, acetylcholine and its derivatives have been extensively studied to improve our understanding of the function of the cholinergic nervous system. Crystallographic studies of salts of acetylcholine and related compounds (Jensen, 1984) have been performed in order to analyse the conformations of the compounds and their intermolecular contacts. These contacts may be related to the interactions which occur at the receptor site. The crystal structure of ethoxycarbonylcholine picrate hemihydrate (ETCOPI) has been examined as a part of these studies.



The ethoxycarbonylcholine ion adopts the favoured *gauche* conformation (Jensen, 1984) with the O—C—C—N torsion angle ∓83.60 (9)°. The ethoxycarbonyl moiety adopts an extended conformation with all of the chain torsion angles approximately 180° (Table 2).

The conformation of the picrate ion is very similar to that found in the crystal structure of methoxycarbonylcholine picrate hemihydrate (MECOPI; Frydenvang, Grønborg & Jensen, 1988). O262, O21 and O221 are displaced from the best plane through the benzene ring. O21 is on one side of the plane and the other two O atoms are on the opposite side. The planes of two nitro groups are tilted with respect to the benzene ring, in such a way as to relieve the strain around the phenolate O atom, O21 (Table 2). The third nitro group (N24) is nearly in the plane of the benzene ring. This pattern is in agreement with what is observed for many of the picrate salts found in the Cambridge Structural Database (Version 5.05, April 1993; Allen *et al.*, 1991). Deviations of the atoms from the best plane through the benzene ring are shown in Fig. 1(*b*).

A stereoview of the crystal packing of ETCOPI is shown in Fig. 2. The structure is isomorphous with that of MECOPI and the crystal packing is very similar (see Frydenvang, Grønborg & Jensen, 1988). The phenolate O atom is involved in a hydrogen bond to the water molecule, forming a picrate–water–picrate linkage. The water molecule is situated on a twofold axis. Electrostatic interactions are observed between the carbonyl C atom of the ethoxycarbonyl moiety and two nitro groups of the picrate ions [C2···O222 3.045 (1) and C2···O261 ($x+1, y, z$) 3.053 (1) Å]. The carbonyl C atom has a partial positive charge and O222 approaches the carbonyl group from one side of the planar moiety, and O261 from the opposite side. Furthermore, close contacts are observed between the quaternary ammonium

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