I thank the Bat-Sheva Foundation of Israel for financial support.

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Acta Cryst. (1988). C**44**, 870–872

Structure of 5-Methyl-2′-deoxycytidine

By Tomohiro Sato

Shionogi Research Laboratories, Shionogi & Co. Ltd, Fukushima-ku, Osaka 553, *Japan*

(*Received* 8 *September* 1987; *accepted* 7 *January* 1988)

Abstract. $C_{10}H_{15}N_3O_4$, $M_r = 241{\cdot}2$, orthorhombic, $P2_12_12_1$, $a = 10{\cdot}454\ (1)$, $b = 11{\cdot}922\ (1)$, $c = 9{\cdot}057\ (1)$ Å, $V = 1128{\cdot}9\ (1)$ Å^3, $Z = 4$, $D_x = 1{\cdot}419$ Mg m^{-3}, Cu $K\alpha$ radiation, $\lambda = 1{\cdot}54178$ Å, $\mu = 0{\cdot}95$ mm^{-1}, $F(000) = 512$, room temperature, $R = 0{\cdot}029$ for 1186 observed reflections. The molecule has a typical C(2′)-*endo* (^2E) furanose ring associated with an *anti* base. The methyl substituent at C(5) causes a decrease of 2·6° in the endocyclic bond angle at C(5). The ring oxygen O(4′) is involved in an intermolecular hydrogen bond.

Introduction. Some of the cytosine residues in DNA are reversibly methylated at the C(5) position. Such a methylation causes a profound effect on the conformation of DNA (Behe & Feldsenfeld, 1980) and gene expression (Radin & Riggs, 1980; Ehrlich & Wang, 1981). Consequently, it is of interest to study the stereochemical effect of the substitution. Previous studies on the crystal structures of 5-methylcytosine (Takenaka, Kato & Sasada, 1980) and 5-methylarabinosylcytosine (Birnbaum & Gentry, 1983) have demonstrated a significant deformation of the pyrimidine ring on the substitution.

Experimental. Crystals grown from methanol/acetone, colorless plate, D_m not measured. Crystal dimensions 0·2 × 0·2 × 0·3 mm, Rigaku AFC-5 diffractometer, graphite-monochromated Cu $K\alpha$ radiation. Lattice parameters from 24 reflections ($50 < 2\theta < 58°$). $\omega/2\theta$ scan, $2\theta \le 140°$, $0 \le h \le 12$, $0 \le k \le 14$, $0 \le l \le 11$, three standard reflections: no variation. 1199 independent reflections measured, 1186 with $I \ge 2\sigma(I)$ 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 $g = 0{\cdot}52\ (2) \times 10^{-4}$, $\sum w(\Delta F)^2$ minimized, $w = 1$, $R = 0{\cdot}029$, $wR = 0{\cdot}029$, final $(\text{shift}/\sigma)_{\max} < 0{\cdot}3$, $-0{\cdot}15 \le \Delta\rho \le 0{\cdot}12$ e Å^{-3}. The final atomic parameters are given in Table 1.* Bond distances and angles are listed in Table 2.

All crystallographic computations 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 nucleoside adopts one of the most commonly observed conformations. The pseudorotation coordinates (Sato, 1983) of the furanose ring are $\Pi = 37{\cdot}9\ (3)°$ and $\Phi = 252{\cdot}7\ (4)°$ and, therefore, the

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* Lists of hydrogen-atom parameters, anisotropic thermal parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44672 (11 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. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å² × 10³)

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

	x	y	z	$U_{\rm eq}$
N(1)	0·4372 (2)	0·5433 (2)	0·5833 (2)	32·3 (6)
C(2)	0·4353 (2)	0·5741 (2)	0·7318 (2)	34·9 (7)
N(3)	0·3555 (2)	0·6582 (2)	0·7729 (2)	37·0 (6)
C(4)	0·2818 (2)	0·7100 (2)	0·6737 (3)	33·3 (7)
C(5)	0·2743 (2)	0·6744 (2)	0·5219 (3)	34·0 (7)
C(6)	0·3548 (2)	0·5920 (2)	0·4845 (2)	35·2 (7)
O(2)	0·5061 (2)	0·5255 (2)	0·8186 (2)	55·4 (7)
N(4)	0·2115 (3)	0·7960 (2)	0·7199 (3)	46·0 (8)
C(7)	0·1826 (3)	0·7269 (3)	0·4142 (4)	48 (1)
O(4′)	0·5895 (2)	0·5063 (1)	0·4035 (2)	34·1 (5)
C(1′)	0·5311 (2)	0·4611 (2)	0·5325 (2)	31·7 (7)
C(2′)	0·4770 (2)	0·3490 (2)	0·4846 (3)	36·5 (7)
C(3′)	0·5783 (2)	0·3080 (2)	0·3769 (3)	32·4 (7)
C(4′)	0·6214 (2)	0·4168 (2)	0·3024 (2)	30·6 (7)
O(3′)	0·6859 (2)	0·2606 (2)	0·4504 (2)	41·8 (6)
C(5′)	0·5555 (3)	0·4369 (2)	0·1560 (3)	42·8 (8)
O(5′)	0·5979 (3)	0·5390 (2)	0·0970 (2)	74·6 (9)

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

N(1)—C(2)	1·394 (3)	N(1)—C(6)	1·371 (3)
N(1)—C(1′)	1·461 (3)	C(2)—N(3)	1·356 (3)
C(2)—O(2)	1·225 (3)	N(3)—C(4)	1·335 (3)
C(4)—C(5)	1·441 (3)	C(4)—N(4)	1·329 (4)
C(5)—C(6)	1·337 (4)	C(5)—C(7)	1·504 (4)
O(4′)—C(1′)	1·424 (3)	O(4′)—C(4′)	1·446 (3)
C(1′)—C(2′)	1·515 (4)	C(2′)—C(3′)	1·521 (4)
C(3′)—C(4′)	1·530 (3)	C(3′)—O(3′)	1·424 (3)
C(4′)—C(5′)	1·513 (4)	C(5′)—O(5′)	1·401 (4)
C(2)—N(1)—C(6)	120·6 (2)	C(2)—N(1)—C(1′)	119·4 (2)
C(6)—N(1)—C(1′)	120·0 (2)	N(1)—C(2)—N(3)	118·0 (2)
N(1)—C(2)—O(2)	119·1 (2)	N(3)—C(2)—O(2)	123·0 (2)
C(2)—N(3)—C(4)	120·8 (2)	N(3)—C(4)—C(5)	122·5 (2)
N(3)—C(4)—N(4)	117·6 (2)	C(5)—C(4)—N(4)	119·8 (2)
C(4)—C(5)—C(6)	115·0 (2)	C(4)—C(5)—C(7)	122·1 (2)
C(6)—C(5)—C(7)	122·9 (2)	N(1)—C(6)—C(5)	122·8 (2)
C(1′)—O(4′)—C(4′)	109·8 (2)	N(1)—C(1′)—O(4′)	107·0 (2)
N(1)—C(1′)—C(2′)	115·6 (2)	O(4′)—C(1′)—C(2′)	105·0 (2)
C(1′)—C(2′)—C(3′)	102·0 (2)	C(2′)—C(3′)—C(4′)	102·4 (2)
C(2′)—C(3′)—O(3′)	112·2 (2)	C(4′)—C(3′)—O(3′)	108·0 (2)
O(4′)—C(4′)—C(3′)	106·2 (2)	O(4′)—C(4′)—C(5′)	109·4 (2)
C(3′)—C(4′)—C(5′)	112·8 (2)	C(4′)—C(5′)—O(5′)	109·2 (2)

ring is puckered in a typical C(2′)-*endo* envelope form. The conformations about the glycosyl and the C(4′)—C(5′) bonds are *anti* and *trans–gauche*, the torsion angles O(4′)—C(1′)—N(1)—C(6) and C(3′)—C(4′)—C(5′)—O(5′) being 46·3 (3) and 178·7 (2)°, respectively.

The pyrimidine ring is significantly nonplanar: the ring torsion angles about the bonds N(1)—C(2), C(2)—N(3), ..., C(6)—N(1) are −4·1 (3), −0·4 (5), 5·3 (4), −5·6 (4), 1·0 (4) and 3·7 (4)°, respectively. This deformation can be considered as a bending about the axis passing through N(1) and C(4). However, since the other 5-methylated cytosines cited above show different types of nonplanarity, the observed bending is not characteristic of the methylation but reflects a flexible nature common to pyrimidine bases (Taylor & Kennard, 1982*a*). The most significant changes due to the methylation are a decrease of the bond angle C(4)—C(5)—C(6) by 2·6° and an increase of the bond distance C(4)—C(5) by 0·015 Å, when compared with the averaged values of the unsubstituted cytosine residue (Taylor & Kennard, 1982*b*). Similar changes have been observed for the other 5-methylated cytosines but the elongation of the C(5)—C(6) bond such as found in 5-methylarabinosylcytosine (Birnbaum & Gentry, 1983) is not observed here.

Four available protons in the molecule are all involved in intermolecular hydrogen bonds, *i.e.* N(4)—H(1)···O(5′) [2·834 (4)], N(4)—H(2)···O(4′) [2·904 (3)], O(3′)—H···N(3) [2·822 (3)] and O(5′)—H···O(2) [2·703 (3) Å]. The participation of the ring oxygen O(4′) in hydrogen bonding is rather exceptional for the crystal structures of nucleosides and nucleotides. The packing scheme in the crystal is shown in Fig. 2.

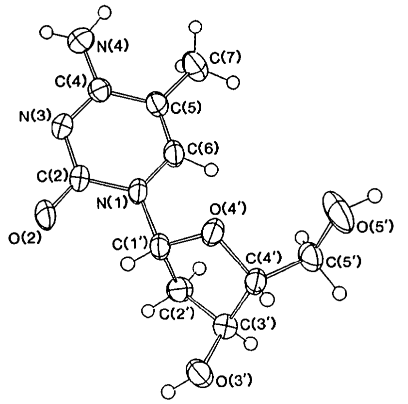

Fig. 1. A perspective view of the molecule with atom-numbering scheme, prepared with *ORTEP* in *XTAL*2.2 (Hall & Stewart, 1987).

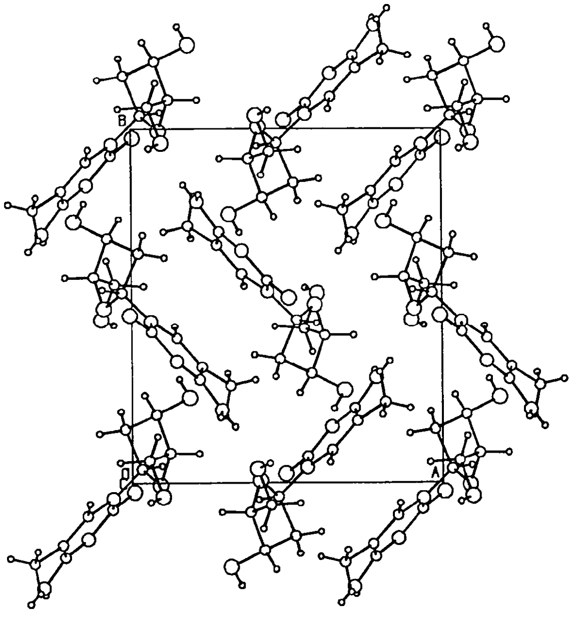

Fig. 2. A [001] projection of the unit cell, prepared with *PLUTO* (Motherwell & Clegg, 1978).

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Acta Cryst. (1988). C**44**, 872–874

Inside-Protonated 1,8-Diazabicyclo[6.5.3]hexadecane Picrate

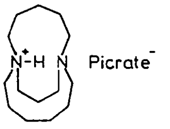
By J. M. White, R. W. Alder and A. G. Orpen

*Departments of Inorganic and Organic Chemistry, The University, Bristol BS*8 1*TS*, *England*

(*Received* 27 *November* 1987; *accepted* 19 *January* 1988)

Abstract. $C_{14}H_{29}N_2^+.C_6H_2N_3O_7^-$, $M_r = 453{\cdot}54$, triclinic, $P\bar{1}$, $a = 8{\cdot}435\,(2)$, $b = 12{\cdot}036\,(2)$, $c = 12{\cdot}630\,(2)$ Å, $\alpha = 62{\cdot}78\,(2)$, $\beta = 86{\cdot}45\,(2)$, $\gamma = 73{\cdot}77\,(2)°$, $V = 1091{\cdot}5\,(4)$ Å^3, $Z = 2$, $D_x = 1{\cdot}38$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 0{\cdot}99$ cm^{-1}, $F(000) = 484$, $T = 293$ K, $R = 0{\cdot}051$ for 1867 unique observed reflections. The title compound has an intrabridgehead N(1)···N(8) distance of 2·610 (5) Å, the inside proton is localized near N(8) with N(8)—H = 1·19 (3), N(1)···H = 1·49 (3) Å and N—H···N = 154 (3)°. The strain imposed by a number of short intramolecular non-bonded H···H contacts is relieved by an expansion in C—C—C angles to a mean value of 116·7 (7)°.

Introduction. Medium-ring bicyclic compounds exhibit many interesting structural and chemical properties (Alder, 1983). The structural study of the title compound (1) is one of a series of studies on the oxidized and protonated ions of medium-ring bicyclic diamines (Alder, Orpen & Sessions, 1983; Alder, Orpen & White, 1985, 1988; White, Alder & Orpen, 1988*a*,*b*). These compounds provide an ideal opportunity to study N—H—N hydrogen bonds of various geometries.



(1)

Table 1. *Atomic coordinates* (× 10^4) *and isotropic thermal parameters* (Å^2 × 10^3)

	x	y	z	U_{eq}*/U
C(17)	1977 (4)	3819 (3)	9425 (3)	52 (2)
C(18)	1626 (4)	3363 (3)	10669 (3)	47 (1)
C(19)	1844 (4)	3956 (3)	11337 (3)	51 (2)
C(20)	2428 (4)	5029 (3)	10836 (3)	49 (2)
C(21)	2776 (4)	5543 (3)	9649 (3)	51 (2)
C(22)	2511 (4)	4976 (3)	8984 (3)	49 (2)
O(1)	1875 (4)	3288 (3)	8809 (2)	86 (2)
O(21)	529 (5)	1826 (3)	10681 (3)	123 (2)
O(22)	822 (5)	1809 (3)	12298 (3)	126 (2)
O(41)	2271 (3)	5213 (3)	12575 (2)	88 (2)
O(42)	3080 (4)	6648 (3)	11044 (3)	99 (2)
O(61)	1737 (4)	5768 (3)	7002 (2)	107 (2)
O(62)	3976 (4)	6006 (3)	7417 (2)	109 (2)
N(2)	966 (4)	2261 (3)	11255 (3)	65 (2)
N(4)	2598 (4)	5671 (3)	11533 (3)	69 (2)
N(6)	2770 (4)	5618 (3)	7707 (2)	67 (2)
N(1)	3485 (3)	248 (3)	7948 (2)	61 (1)
C(2)	5181 (5)	255 (4)	8222 (4)	97 (3)
C(3)	5377 (5)	1588 (4)	7823 (4)	91 (3)
C(4)†	5714 (13)	2482 (11)	6525 (12)	86 (6)
C(5)†	4466 (8)	2838 (6)	5596 (5)	76 (3)
C(6)	2823 (5)	3744 (4)	5651 (4)	89 (2)
C(7)	1562 (7)	3320 (4)	5268 (4)	112 (3)
N(8)	1320 (4)	2081 (3)	6216 (2)	68 (2)
C(9)	593 (6)	1414 (4)	5681 (4)	94 (3)
C(10)	1866 (7)	694 (5)	5142 (4)	107 (3)
C(11)	2739 (6)	−717 (4)	5929 (4)	91 (3)
C(12)	4101 (5)	−1069 (4)	6835 (4)	96 (3)
C(13)	3542 (5)	−997 (4)	7974 (4)	88 (2)
C(14)	2290 (5)	494 (4)	8804 (3)	82 (2)
C(15)	547 (5)	1059 (4)	8265 (4)	86 (3)
C(16)	284 (5)	2298 (4)	7135 (4)	86 (3)
C(5′)‡	4884 (25)	3436 (19)	5764 (15)	113 (11)
C(4′)‡	5558 (25)	1865 (18)	6552 (19)	80 (9)
H(1)	2540 (45)	1313 (36)	6818 (32)	112 (12)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

† Occupancy 0·658 (5).

‡ Occupancy 0·342 (5).

Experimental. Yellow rod (0·9 × 0·20 × 0·05 mm) from solvent diffusion using CH_2Cl_2 and diethyl ether; Nicolet *P*3*m* diffractometer, 22 reflections centred ($12 < \theta < 13°$), graphite-monochromated Mo *Kα* for data collection, $2 < \theta < 25°$, room temperature, ω–2θ scans in 96 steps, ω scan width $1{\cdot}0 + 0{\cdot}35\tan\theta°$, data measured over 127 X-ray hours with no detectable

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