

## 1-Methylcytosine: A Refinement

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**Abstract.** 1-Methylcytosine,  $C_5N_3OH_7$ , triclinic, space group  $P\bar{1}$ , with  $a = 6.088$  (1),  $b = 6.819$  (3),  $c = 7.038$  (2) Å,  $\alpha = 94.32$  (3),  $\beta = 84.44$  (2),  $\gamma = 99.64$  (2)°,  $V = 286.14$  Å<sup>3</sup>,  $Z = 2$ ,  $M_r = 125.13$ ,  $D_m = 1.448$  (3),  $D_c = 1.452$  g cm<sup>-3</sup>. Full-matrix least-squares refinement (nonhydrogen atoms anisotropic, H atoms isotropic) based on 1191 counter-collected  $F_o$ 's has led to a final  $R$  value of 0.045 and a final weighted  $R$  value of 0.047. As found by Mathews & Rich [*Nature* (1964), **201**, 179–180], the structure consists of extensively hydrogen-bonded molecules, with significant base stacking along the  $b$  axis. In one of the sets of hydrogen-bonded dimers, the molecular planes are shifted relative to each other by 1.41 Å; the absence of coplanarity in this base pairing causes one of the amino H atoms to lie 0.34 Å out of the mean plane of the molecule in order to maximize the hydrogen-bonding interaction.

**Introduction.** The crystal structure of 1-methylcytosine shows one of the most interesting packing motifs exhibited by an alkylated pyrimidine or purine base. The structure was first investigated by Mathews & Rich (1964), based on film data and a somewhat limited set of  $F_o$ 's. Our recent interest in employing 1-methylcytosine as a model for the bonding of cytidine to transition-metal complexes (Marzilli, Kistenmacher & Rossi, 1977) plus the intrinsic interest in the details of the packing motif exhibited by 1-methylcytosine has prompted us to reinvestigate the structure of 1-methylcytosine, employing an extensive set of counter-collected data.

Crystals of 1-methylcytosine were grown from ethanol/water solution at room temperature. The crystal used in our diffractometer study was a parallelepiped with the following dimensions: (100)–( $\bar{1}00$ ) 0.23 mm, (010)–( $0\bar{1}0$ ) 0.13 mm, (001)–( $00\bar{1}$ ) 0.27 mm; the crystal was mounted approximately along the  $c^*$  axis. Precise cell dimensions and their associated standard deviations were obtained from a least-squares fit to the setting angles of 15 carefully centered reflections and are comparable with the values determined by Mathews & Rich (1964).

3009 intensities (the full sphere to  $2\theta = 55^\circ$ ) were measured on a Syntex  $P\bar{1}$  automated diffractometer using Mo  $K\alpha$  graphite-monochromated radiation. The intensity data were collected in the  $\theta$ – $2\theta$  scan mode;

individual scan speeds were determined by a rapid scan at the calculated Bragg peak, and the rate of scanning ( $2\theta$ ) ranged from 1.5° min<sup>-1</sup> (less than 100 counts during the rapid scan) to 24° min<sup>-1</sup> (more than 1000 counts during the rapid scan). All intensities were assigned observational variances based on the equation:  $\sigma^2(I) = S + (B_1 + B_2)(T_s/2T_B)^2 + (pI)^2$ , where  $S$ ,  $B_1$  and  $B_2$  are the scan and extremum background counts,  $T_s$  and  $T_B$  are the scan and extremum background counting times ( $T_B = T_s/4$  for all reflections), and  $p$  was taken to be 0.03 (the maximum deviation of any standard, three of which were taken after every 100 observations, was 3%). The intensities and their standard deviations were corrected for Lorentz, polarization and absorption effects [ $\mu = 1.16$  cm<sup>-1</sup>, maximum and minimum transmission factors (on  $I$ ) of 0.986 and 0.975]. The amplitudes of reflections with  $I \leq 0.2\sigma(I)$  were set equal to zero. The data were then averaged to yield 1193 independent values [136 reflections with  $I_{AVE} \leq (\sigma_{AVE})/n$ , where  $n$  is the number of independent observations contributing to the average, were considered statistically unobserved and removed from the data set].

The refinement was initiated from the final positional parameters of Mathews & Rich (1964) with isotropic thermal parameters of 3.0 Å<sup>2</sup> assigned to all the nonhydrogen atoms. Two cycles of isotropic refinement [minimizing the quantity  $\sum w(|F_o| - |F_c|)^2$ , where  $w = 4F_o^2/\sigma^2(F_o^2)$ ] plus one cycle of anisotropic refinement reduced the  $R$  value [ $\sum ||F_o| - |F_c||/\sum |F_o|$ ] to 0.12. A difference-Fourier synthesis permitted the positioning of the H atoms. The refinement was continued adding to the parameter list: (1) positional parameters for the H atoms, (2) isotropic thermal factors for the H atoms. In these last cycles, the 020 and 1 $\bar{2}$ 0 reflections were excluded, as they were obviously severely affected by secondary extinction. Four cycles in such a mode led to convergence (the shift/error for any parameter was less than 0.25) and a final  $R$  value of 0.045. The final weighted  $R$  value  $\{[\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}\}$  and goodness-of-fit  $\{[\sum w(|F_o| - |F_c|)^2/(\text{NO} - \text{NV})]^{1/2}$ , where NO = 1191 and NV = 110 variables} were 0.047 and 2.4 respectively. A final difference-Fourier map showed no features larger than  $\pm 0.17 e \text{ \AA}^{-3}$ .

The scattering curves for the nonhydrogen atoms were taken from the compilation of Hanson, Herman, Lea & Skillman (1964), while the scattering curve for H

Table 1. *Atomic coordinates* ( $\times 10^4$  for nonhydrogen atoms and  $\times 10^3$  for hydrogen atoms)

Estimated standard deviations are in parentheses.

	<i>x</i>	<i>y</i>	<i>z</i>
O(2)	6621 (2)	2957 (2)	9169 (1)
N(1)	3859 (2)	2223 (2)	7174 (1)
N(3)	7625 (2)	3284 (2)	6000 (1)
N(4)	8540 (2)	3560 (2)	2795 (2)
C(1)	2219 (3)	1821 (3)	8819 (2)
C(2)	6100 (2)	2831 (2)	7507 (2)
C(4)	6986 (2)	3070 (2)	4228 (2)
C(5)	4731 (2)	2346 (2)	3851 (2)
C(6)	3246 (2)	1988 (2)	5357 (2)
H(1)	251 (3)	62 (3)	942 (2)
H(2)	244 (3)	306 (3)	974 (2)
H(3)	78 (4)	164 (3)	837 (3)
H(4)	982 (3)	436 (3)	310 (2)
H(41)	811 (3)	351 (2)	167 (2)
H(5)	433 (3)	220 (2)	265 (2)
H(6)	170 (3)	160 (2)	524 (2)

was that of Stewart, Davidson & Simpson (1965). The real part of the scattering curves for all nonhydrogen atoms was corrected for anomalous dispersion effects (Cromer & Liberman, 1970). Final atomic parameters are collected in Table 1.\*

The structure-factor and least-squares calculations were carried out with an extensively modified version of *ORFLS* (Busing, Martin & Levy, 1962); Fourier maps were computed with *FORDAP* (Zalkin, 1965); the absorption correction was applied using *ORABS* (Wehe, Busing & Levy, 1962); best planes were computed with *MEAN PLANE* (Pippy & Ahmed, 1968); illustrations were prepared with the aid of *ORTEP* (Johnson, 1965). Calculations not cited were performed with locally written programs.

**Discussion.** Our refinement of the structure of 1-methylcytosine has led to a more precise result that is in

\* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32937 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

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

N(1)–C(2)	1.395 (2)	C(5)–C(6)	1.334 (2)
C(2)–N(3)	1.358 (2)	N(1)–C(6)	1.357 (2)
N(3)–C(4)	1.332 (2)	N(1)–C(1)	1.464 (2)
C(4)–C(5)	1.422 (2)	C(2)–O(2)	1.234 (2)
		C(4)–N(4)	1.336 (2)
C(2)–N(1)–C(6)	120.1 (1)	C(1)–N(1)–C(6)	121.5 (1)
N(1)–C(2)–N(3)	118.0 (1)	C(1)–N(1)–C(2)	118.5 (1)
C(2)–N(3)–C(4)	120.0 (1)	N(1)–C(2)–O(2)	118.6 (1)
N(3)–C(4)–C(5)	121.8 (1)	N(3)–C(2)–O(2)	122.4 (1)
C(4)–C(5)–C(6)	117.2 (1)	N(3)–C(4)–N(4)	117.8 (1)
C(5)–C(6)–N(1)	121.8 (1)	N(4)–C(4)–C(5)	120.4 (1)

accord with previous structural data on cytosine derivatives (Voet & Rich, 1970). We present in Table 2 our derived bond lengths and angles and in Fig. 1 an illustration of the 1-methylcytosine molecule and its thermal ellipsoids.

In accord with the original results of Mathews & Rich (1964), we find two types of hydrogen-bond dimers (Fig. 2). The parameters in these interbase hydrogen bonds are as follows: N(4)–H(4)⋯N(3)[ $2 - x, 1 - y, 1 - z$ ], N(4)⋯N(3) 3.038 (2) Å,

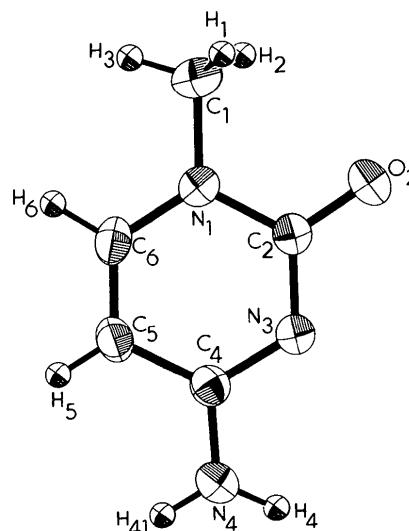


Fig. 1. The 1-methylcytosine molecule viewed along the normal to the mean plane of the six-atom framework. The thermal ellipsoids of the nonhydrogen atoms are drawn at the 50% probability level. The isotropic thermal parameters for the H atoms have been artificially set to  $1.0 \text{ \AA}^2$ .

Table 3. *Mean plane of the 1-methylcytosine molecule and deviations of atoms* (Å)

The equation of the mean plane of the 1-methylcytosine ring is:  $0.3229X - 0.9441Y - 0.0662Z = -0.6074 \text{ \AA}$ , where  $X$ ,  $Y$  and  $Z$  are coordinates (Å) referred to the orthogonal axes  $X$  along  $a$ ,  $Y$  in the  $ab$  plane and  $Z$  along  $c^*$ . Atoms designated with an asterisk were given zero weight in the calculation of the plane; all other atoms were equally weighted.

N(1)	-0.016 (1)	N(4)	-0.061 (1)*
N(3)	-0.006 (1)	C(1)	-0.042 (1)*
C(2)	0.022 (1)	H(4)	-0.34 (2)*
C(4)	-0.016 (1)	N(3')†	-1.408 (1)*
C(5)	0.022 (1)	H(41)	-0.13 (2)*
C(6)	-0.006 (1)	O(2')‡	-0.090 (1)*
O(2)	0.066 (1)*	H(5)	0.02 (2)*
		H(6)	-0.05 (2)*

† N(3') is related to N(3) by the transformation  $2 - x, 1 - y, 1 - z$ ; N(3') is hydrogen bonded to H(4).

‡ O(2') is related to O(2) by the transformation  $x, y, -1 + z$ ; O(2') is hydrogen bonded to H(41).

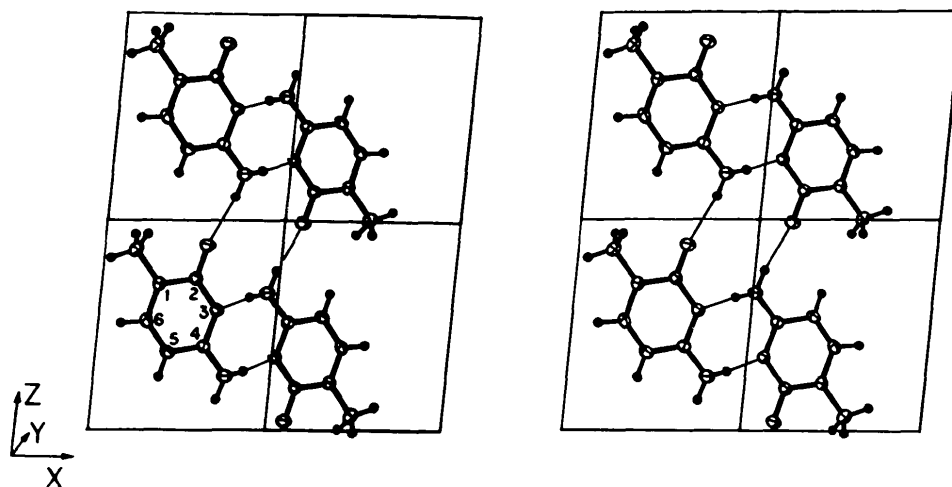


Fig. 2. A stereoview of the hydrogen-bonding interactions in the 1-methylcytosine structure. The numbered molecule has the coordinates as given in Table 1.

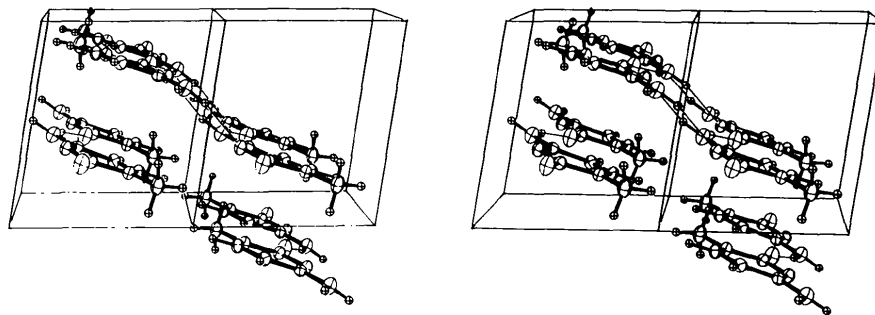


Fig. 3. A complete stereoview of the crystal packing in 1-methylcytosine. The view direction is along the  $-c^*$  axis. Note the nonplanarity of one set of the hydrogen-bonded bases.

$\text{H}(4)\cdots\text{N}(3)$  2.14 (2) Å,  $\angle\text{N}(4)\text{—H}(4)\cdots\text{N}(3)$  167 (1)°;  $\text{N}(4)\text{—H}(41)\cdots\text{O}(2)[x, y, -1+z]$ ,  $\text{N}(4)\cdots\text{O}(2)$  2.882 (2) Å,  $\text{H}(41)\cdots\text{O}(2)$  2.04 (2) Å,  $\angle\text{N}(4)\text{—H}(41)\cdots\text{O}(2)$  169 (1)°. In the hydrogen-bond dimers of the first type involving  $\text{N}(4)\text{—H}(4)$  and  $\text{N}(3)$ , the two bases are remarkably non-coplanar (Figs. 2 and 3) with a mean separation of 1.41 Å (Table 3). In order to maximize the interbase hydrogen bonding in this pair, the amino hydrogen  $\text{H}(4)$  lies 0.34 Å out of the mean plane of the cytosine residue toward the acceptor  $\text{N}(3)$  to which it is hydrogen bonded (Table 3). We know of no other system in which a H atom on a purine or pyrimidine base has adjusted its position so drastically in order to yield the best hydrogen-bond interaction.

A second important packing effect in the structure of 1-methylcytosine lies in the formation of columnar stacks along the  $b$  axis (Fig. 3). Two types of molecular overlap occur within these columns; as observed in many molecular systems, the mode of stacking in each

case is of the ring-bond type (Bugg, Thomas, Sundaralingam & Rao, 1971; Herbstein, 1971).

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### Tetrakis[acetatotriphenylphosphinesilver(I)]

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**Abstract.**  $C_{80}H_{72}O_8P_4Ag_4$ ,  $M_r = 1716.0$ , monoclinic, space group  $P2_1/c$  (systematic absences  $h0l, l = 2n + 1, 0k0, k = 2n + 1$ ),  $a = 13.616$  (11),  $b = 12.436$  (12),  $c = 23.489$  (17) Å,  $\beta = 91.28$  (11)°,  $U = 3976.4$  Å<sup>3</sup>,  $Z = 2$ ,  $d_m = 1.43$  (1),  $d_c = 1.43$  g cm<sup>-3</sup>, Mo  $K\alpha$  radiation,  $\lambda = 0.7107$  Å,  $\mu(\text{Mo } K\alpha) = 10.7$  cm<sup>-1</sup>. In the centrosymmetric tetramer, the two independent Ag atoms have different environments. One is bonded to a triphenylphosphine [Ag–P 2.376 (3) Å] and to two O atoms [2.241 (8), 2.260 (10) Å] while the other is

bonded to a triphenylphosphine [2.354 (3) Å] and to three O atoms [2.226 (12), 2.320 (7), 2.475 (7) Å]. 2895 independent reflexions measured by counter methods have been refined to  $R = 0.067$ .

**Introduction.** Crystals of  $[Ag(PPh_3)(O_2CMe)]_4$  were prepared by reaction of  $AgO_2CMe$  with an equimolar amount of  $PPh_3$  in toluene at reflux followed by filtration of the hot solution and recrystallization by slow evaporation of the same solvent. A crystal with

Table 1. Final positional parameters ( $\times 10^4$ ) with estimated standard deviations in parentheses

	x	y	z		x	y	z
Ag(1)	6137 (1)	4821 (1)	4592 (0)	C(23)	8407 (10)	5603 (11)	1875 (6)
Ag(2)	6974 (1)	6974 (1)	4120 (0)	C(24)	7473 (12)	5441 (13)	1736 (7)
P(1)	6441 (2)	3568 (2)	3865 (1)	C(25)	6725 (10)	5784 (12)	2067 (6)
P(2)	8170 (2)	7139 (3)	3405 (1)	C(26)	6911 (9)	6256 (10)	2583 (5)
C(1)	4700 (8)	6831 (9)	4358 (5)	C(32)	9465 (9)	5974 (10)	4066 (5)
O(1)	4857 (5)	6041 (7)	4666 (3)	C(33)	10396 (10)	5668 (12)	4270 (6)
O(2)	5346 (6)	7225 (7)	4046 (4)	C(34)	11246 (9)	6154 (10)	4051 (6)
C(2)	3720 (9)	7388 (10)	4366 (5)	C(35)	11167 (9)	6877 (11)	3644 (6)
O(3)	7149 (7)	7265 (8)	5067 (4)	C(36)	10245 (9)	7237 (10)	3421 (5)
C(3)	7261 (9)	6486 (12)	5381 (6)	C(42)	5801 (9)	2999 (11)	2751 (6)
O(4)	7221 (8)	5564 (10)	5196 (5)	C(43)	5212 (11)	3146 (12)	2270 (6)
C(4)	7442 (12)	6653 (14)	6009 (8)	C(44)	4620 (10)	3933 (12)	2268 (6)
C(11)	8356 (7)	8491 (8)	3168 (4)	C(45)	4506 (12)	4649 (14)	2626 (8)
C(21)	7935 (7)	6430 (8)	2763 (4)	C(46)	5122 (9)	4537 (11)	3169 (6)
C(31)	9383 (8)	6766 (9)	3667 (5)	C(52)	5113 (8)	2105 (10)	4246 (5)
C(41)	5778 (7)	3763 (9)	3211 (5)	C(53)	4764 (10)	1028 (11)	4377 (6)
C(51)	6061 (7)	2222 (8)	4037 (4)	C(54)	5331 (10)	190 (11)	4280 (6)
C(61)	7727 (8)	3471 (9)	3682 (4)	C(55)	6262 (11)	299 (13)	4095 (7)
C(12)	8334 (10)	8811 (10)	2634 (5)	C(56)	6648 (9)	1321 (11)	3959 (5)
C(13)	8293 (10)	9921 (11)	2453 (6)	C(62)	8079 (8)	3703 (9)	3134 (5)
C(14)	8645 (9)	10621 (10)	2852 (6)	C(63)	9103 (9)	3633 (11)	3030 (5)
C(15)	8867 (10)	10308 (12)	3389 (6)	C(64)	9723 (10)	3352 (11)	3456 (6)
C(16)	8698 (9)	9268 (11)	3550 (5)	C(65)	9393 (9)	3103 (11)	4011 (6)
C(22)	8669 (9)	6093 (10)	2386 (6)	C(66)	8366 (8)	3195 (10)	4121 (5)