

## 1-Methyl-5-fluoro-6-methoxy-5,6-dihydrouracil

BY M. N. G. JAMES\* AND M. MATSUSHIMA

Department of Biochemistry, University of Alberta, Edmonton, Alberta, T6G 2H7, Canada

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**Abstract.**  $C_6H_9FN_2O_3$ , M.W. 176.15, tetragonal,  $I4_1/a$ ,  $a=b=21.102$  (3),  $c=7.141$  (1) Å,  $D_m=1.49$ ,  $D_x=1.47$  g cm<sup>-3</sup>,  $Z=16$ . The final  $R$  was 0.042 for 1298 reflexions [ $I > 3\sigma(I)$ ]. The configuration of the product from the addition of methyl hypofluoride to the C(5)=C(6) bond of 1-methyluracil is *cis*.

**Introduction.** Crystals were supplied by Dr M. J. Robins, Chemistry Department, University of Alberta (Robins & Naik, 1971). Weissenberg and oscillation photographs revealed that the crystals were tetragonal, space group  $I4_1/a$ . Possible reflexions were limited by:  $00l: l=4n$ ;  $hk0: h$  or  $k=2n$ ;  $hkl: h+k+l=2n$ . A single crystal,  $0.4 \times 0.4 \times 0.3$  mm, was mounted on a Picker FACS-1 diffractometer and graphite-monochromatized Mo  $K\alpha$  radiation ( $\lambda=0.70926$  Å) used to collect intensities up to  $2\theta=55^\circ$  by the  $\theta-2\theta$  scan mode. The number of reflexions with  $I > 3\sigma(I)$ ,  $\sigma(I)=(\text{total count})^{1/2}$ , was 1298 out of the 1841 reflexions scanned. These 1298 reflexions were included in the refinement. The intensities were reduced to structure amplitudes by the application of Lorentz-polarization corrections.

The structure amplitudes were converted to normalized structure factors by a Wilson (1942) plot ( $B=3.75$  Å<sup>2</sup>) and the structure was solved by direct methods (Karle & Karle, 1966). The refinement, unit weights, was carried out by full-matrix least squares. The final

$R$  was 0.042.† The scattering factors for C, N, O and F were taken from Cromer & Mann (1968) and for H from Stewart, Davidson & Simpson (1965). The programs used were from the X-RAY 70 system (*SIGMA2* was modified for the tetragonal system by M.M.) (Stewart, Kundell & Baldwin, 1970). The atomic parameters are listed in Table 1.

The atomic numbering and the bond lengths and angles are shown in Fig. 1.

**Discussion.** The title compound was synthesized by the addition of methyl hypofluoride to 1-methyluracil in trichlorofluoromethane. The primary object of this study was to determine whether the configuration of the product was *cis* or *trans*. The analysis shows that the configuration is *cis* with respect to the substituents on C(5)=C(6) in 1-methyluracil (Fig. 2).

Although the bond lengths of this compound agree closely with those of dihydrouracil (Rohrer & Sundaralingam, 1970), the bond angles agree with those of dihydrothymine (Furberg & Jensen, 1968) and dihydrothymidine (Konnert, Karle & Karle, 1970). C(2)-N(3), 1.397 (3), is longer than N(1)-C(2), 1.347 (3), and N(3)-C(4), 1.357 (3) Å. This tendency has been observed in all the dihydrouracil derivatives.

\* On leave at the Department of Structural Chemistry, Weizmann Institute of Science, Rehovot, Israel.

† A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31495 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Positional and thermal parameters

(a) The parameters ( $\times 10^4$ ) of the non-hydrogen atoms

The anisotropic temperature factor parameters  $U_{ij}$  are in the form:  $T = \exp [-2\pi^2(U_{11}h^2a^{*2} + \dots + 2U_{12}hka^*b^* + \dots)]$ .

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
N(1)	1551 (1)	2215 (1)	4373 (3)	289 (9)	363 (9)	422 (11)	-19 (7)	-11 (8)	-63 (8)
C(2)	937 (1)	2364 (1)	4118 (3)	320 (10)	385 (11)	396 (12)	-22 (8)	-2 (9)	-32 (10)
N(3)	548 (1)	1887 (1)	3396 (3)	297 (9)	372 (10)	527 (12)	-24 (7)	-43 (9)	-57 (9)
C(4)	756 (1)	1352 (1)	2543 (3)	478 (12)	345 (11)	343 (11)	-20 (9)	-78 (10)	22 (9)
C(5)	1462 (1)	1364 (1)	2197 (3)	504 (13)	351 (11)	359 (11)	46 (10)	53 (10)	-44 (10)
C(6)	1787 (1)	1580 (1)	3967 (3)	315 (11)	405 (11)	406 (12)	23 (9)	28 (9)	6 (10)
C(1)	1974 (1)	2712 (1)	5043 (5)	339 (13)	519 (16)	765 (22)	-48 (11)	-85 (14)	-176 (15)
O(2)	713 (1)	2884 (1)	4490 (3)	328 (8)	406 (9)	724 (13)	26 (7)	-26 (8)	-149 (9)
O(4)	408 (1)	922 (1)	2077 (3)	607 (11)	390 (9)	615 (12)	-101 (8)	-157 (9)	-35 (8)
F(5)	1665 (1)	766 (1)	1678 (2)	723 (10)	482 (8)	595 (10)	108 (7)	72 (8)	-155 (8)
O(6)	1629 (1)	1132 (1)	5336 (2)	445 (9)	499 (10)	403 (9)	-12 (7)	-50 (7)	69 (8)
C(7)	1954 (2)	1206 (2)	7072 (5)	647 (21)	1056 (30)	439 (17)	-32 (20)	-134 (16)	97 (18)

Table 1 (cont.)

(b) The parameters ( $\times 10^3$ ) of the hydrogen atoms

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>iso</sub>
H(3)	14 (1)	194 (1)	361 (4)	56 (8)
H(5)	158 (1)	166 (1)	112 (4)	47 (7)
H(6)	226 (1)	162 (1)	384 (3)	35 (6)
H(11)	193 (2)	307 (2)	432 (6)	118 (15)
H(12)	239 (2)	256 (2)	510 (5)	83 (11)
H(13)	185 (2)	285 (2)	630 (6)	116 (15)
H(71)	199 (1)	66 (2)	773 (5)	91 (11)
H(72)	178 (2)	153 (2)	776 (7)	156 (20)
H(73)	241 (2)	124 (2)	696 (6)	119 (15)

The torsion angles are shown in Fig. 3. O(4)=C(4)-C(5)-F(5) is  $13.5^\circ$ . Such small torsional angles between electronegative atoms were found in monochloro- (Ichikawa, 1972) and monofluoro-acetic acid (Kanters & Kroon, 1972). The torsion angle about C(5)-C(6) corresponds to the perfect staggered conformation notwithstanding the fact that the present compound has part of the six-membered ring involved in a conjugated system.

O(6)-C(6), 1.401 (3), is shorter than O(6)-C(7), 1.425 (4) Å. The torsion angle C(7)-O(6)-C(6)-N(1) is  $70.6^\circ$ . A similar trend in these bond lengths was found in the C-O-C-O system of saccharides (Berman, Chu & Jeffrey, 1967). Jeffrey, Pople & Radom (1972) found that the total energy of methylenediol was minimized at a torsion angle of  $59.7^\circ$ . This conformational stability had been termed the anomeric effect (Lemieux & Chü, 1958). Similar to the C-O-C-O system, the trend in bond lengths and the conformation in the system C-O-C-N could be due to the anomeric effect.

Two hydrogen bonds produce a dimer-like unit in which two molecules are related by twofold symmetry in an inversion tetrad axis (Fig. 2). The interatomic distances are 1.95 (3) between H(3) and O(2<sup>1</sup>) and 2.814 (2) Å between N(3) and O(2<sup>1</sup>). The angles are

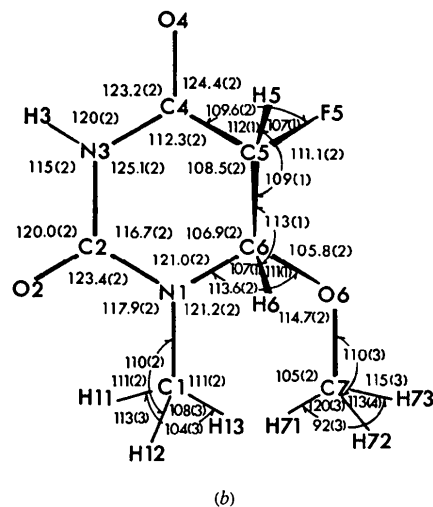
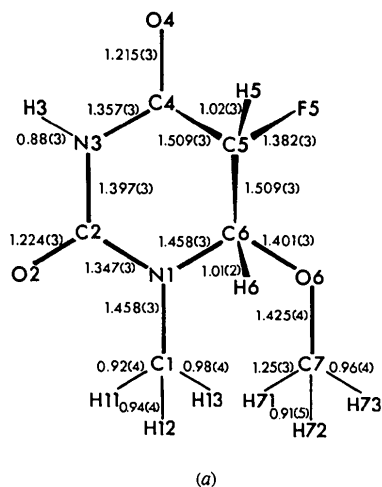
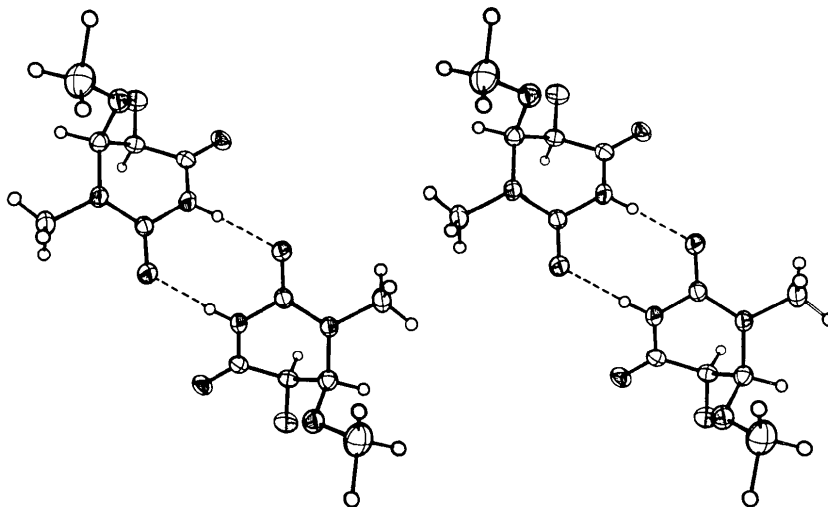
Fig. 1. (a) Bond lengths (Å). (b) Bond angles ( $^\circ$ ).

Fig. 2. Stereoscopic diagram of the dimer-like unit of 1-methyl-5-fluoro-6-methoxy-5,6-dihydrouracil (Johnson, 1965).

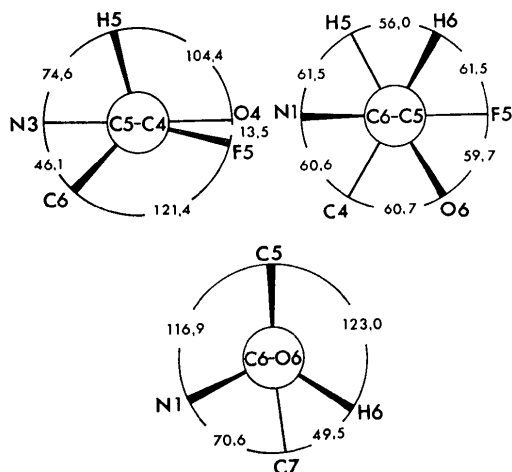


Fig. 3. Torsion angles in the form of Newman projections.

170 (3) for  $N(3)-H(3)\cdots O(2^i)$  and  $117.3(8)^\circ$  for  $C(2)-O(2)\cdots H(3^i)$ . The symmetry operation,  $i$ , is at  $(\frac{1}{2}-x, y, z)$ .

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## N-Succinopyridine

BY M. N. G. JAMES\* AND M. MATSUSHIMA

*Department of Biochemistry, University of Alberta, Edmonton, Alberta, T6G 2H7, Canada*

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**Abstract.**  $C_9H_9NO_4$ , M.W. 195.17, orthorhombic,  $P2_12_12_1$ ,  $a=7.775(2)$ ,  $b=14.974(3)$ ,  $c=7.730(2)$  Å,  $Z=4$ ,  $D_m=1.442$ ,  $D_x=1.439$  g cm $^{-3}$ . The final  $R$  was 0.032 for 1037 reflexions [ $I>3\sigma(I)$ ]. The molecular dimensions agree well with the aspartic acid structures. In the crystals the carbonyl and the negatively charged O atoms approach the positions *ortho* and *para* with respect to the N atom of the pyridinium moiety.

**Introduction.** Unexpectedly, maleic acid reacts with pyridine in water to produce *N*-succinopyridine. Oscillation and Weissenberg photographs showed that the crystals belonged to the space group  $P2_12_12_1$ . The systematic absences were:  $h00: h=2n+1$ ;  $0k0: k=2n+1$ ;  $00l: l=2n+1$ . A single crystal,  $0.23\times 0.25\times 0.43$  mm, was mounted on a Picker FACS-1 diffractometer and

graphite-monochromatized Mo  $K\alpha$  radiation ( $\lambda=0.70926$  Å) was used to measure intensities up to  $2\theta=55^\circ$  by  $\theta-2\theta$  scan mode for  $hkl$  and  $hk\bar{l}$  reflexions. After averaging these two independent sets, 1037 out of 1221 reflexions had  $I>3\sigma(I)$ . The intensities were reduced to structure amplitudes by the Lorentz and polarization factors and then to  $E$ 's by a Wilson (1942) plot ( $B=3.21$  Å $^2$ ). The structure was solved by direct methods (Karle & Karle, 1966). The atomic parameters, arbitrarily describing the *L*-enantiomer, were refined by full-matrix least squares. The weighting scheme was  $w=[2|F_o|^{1/2}/\sigma(I)]$ . The final  $R$  and  $R_w$  were 0.032 and 0.031, respectively.† The maximum shift for the non-

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