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A modification of a previously reported synthesis of 1-methyluracil which simplifies the isolation of the compound is reported together with a refined X-ray analysis of the title compound.

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1-Methyluracil, $C_5H_6N_2O_2$, represents a model for the naturally occurring nucleobase uridine and thymidine, respectively. In the course of studies on the interaction of transition metal ions and in particular of platinum group metals with model nucleobases, we are utilizing 1-methyluracil extensively [1].

The synthesis of 1-methyluracil from 2-thiouracil [2] or uracil [3] has been reported before and its crystal structure has been determined [4]. In order to permit a more accurate estimation of the effects of (multiple) metal binding on the geometry of the heterocyclic ring, we decided to re-determine the X-ray structure of 1-methyluracil. At the same time we found that a modification of the method of preparation reported by Sakai *et al.* [3] as well as by Kistenmacher *et al.* [5] (for 1-methylcytosine) simplified the procedure and increased the yield.

Table 1

Atomic Coordinates and Temperature Factors of
1-Methyluracil $C_5H_6N_2O_2$

Atom	X	Y	Z	U
N1	0.2133(1)	0.1266(1)	0.5000(0)	0.016(1)
C1'	0.1030(1)	0.1199(1)	0.5000(0)	0.026(1)
C2	0.2669(1)	0.0371(1)	0.5000(0)	0.016(1)
O2'	0.2253(1)	-0.0459(1)	0.5000(0)	0.022(1)
N3	0.3707(1)	0.0472(1)	0.5000(0)	0.016(1)
C4	0.4249(1)	0.1371(1)	0.5000(0)	0.016(1)
O4'	0.5188(1)	0.1350(1)	0.5000(0)	0.020(1)
C5	0.3634(1)	0.2273(1)	0.5000(0)	0.018(1)
C6	0.2615(1)	0.2186(1)	0.5000(0)	0.016(1)
H1'	0.0809(10)	0.0854(10)	0.6210(23)	0.040(3)
H1''	0.0827(14)	0.1895(15)	0.5000(0)	0.030(4)
H3	0.4093(13)	-0.0139(14)	0.5000(0)	0.023(3)
H5	0.3988(12)	0.2945(14)	0.5000(0)	0.020(3)
H6	0.2127(13)	0.2784(14)	0.5000(0)	0.023(3)

Table 2

Bond Distances (Å) and Angles (deg) of $C_5H_6N_2O_2$

N1 - C1'	1.460(1)	C1' - N1 - C6	121.2(1)
C1' - H1'	0.929(14)	C1' - N1 - C2	117.4(1)
C1' - H1''	0.958(20)	C6 - N1 - C2	121.4(1)
N1 - C2	1.378(1)	O2' - C2 - N1	122.4(1)
C2 - O2'	1.225(1)	O2' - C2 - N3	122.3(1)
C2 - N3	1.378(1)	N1 - C2 - N3	115.3(1)
N3 - H3	0.954(19)	C2 - N3 - C4	126.7(1)
N3 - C4	1.385(1)	O4' - C4 - N3	119.9(1)
C4 - O4'	1.241(1)	O4' - C4 - C5	125.5(1)
C4 - C5	1.441(1)	N3 - C4 - C5	114.6(1)
C5 - H5	1.003(18)	C4 - C5 - C6	119.4(1)
C5 - C6	1.352(1)	C5 - C6 - N1	122.5(1)
C6 - H6	1.109(19)		
C6 - N1	1.370(1)		

Table 3

Crystallographic Data for 1-Methyluracil, $C_5H_6N_2O_2$

fw	126.12
space group	Ibam
a, Å	13.211(5)
b, Å	13.201(4)
c, Å	6.245(1)
V, Å ³	1089.12
Z	4
d _c , gcm ⁻³	1.538
μ, cm ⁻¹	0.78
scan mode	θ/2θ
θ _{range} , deg	36
no of unique refl.	1297
no of refl. used in the calculations	1209 (F _o > 2σF _o)
R	0.047
R _w (F)	0.053 (w ⁻¹ = σ ² (F) + 0.0007 F ²)

Crystals of 1-methyluracil were grown by slow evaporation of an aqueous solution of 1-methyluracil at room temperature. Positional parameters and temperature factors as well as interatomic distances and angles are given in Tables 1 and 2, the molecular structure is depicted in Figure 1. Molecular dimensions of 1-methyluracil are close to those obtained from a neutron diffraction study on 1-methylthymine [6] and within the range reported for a large series of related compounds [7]. Hydrogen bonding between 1-methyluracil rings is as reported by Green *et al.* [4], with centrosymmetric units connected through N(3)H and O(4).

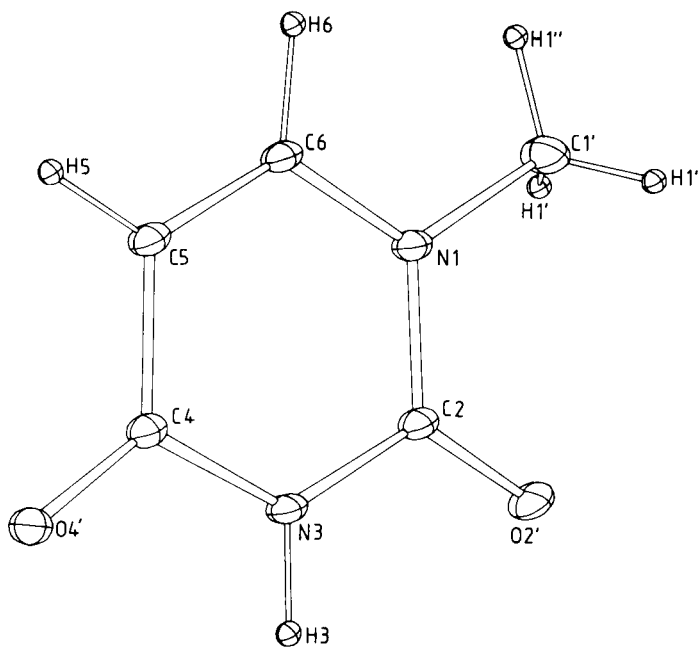


Figure 1. Molecular Structure and atom numbering of 1-methyluracil.

EXPERIMENTAL

Uracil (5.61 g, 50 mmoles), hexamethyldisilazane, HMDS (100 ml), and trimethylchlorosilane, TMCS (9.5 ml) were refluxed at 140° for approximately 5 hours until the reaction mixture became transparent. After cooling the solution to 60°, methyl iodide (30 ml, 0.48 mole) was added and the reaction mixture again refluxed for 38 hours at 60°. To the cold (0°) solution, acetic acid (200 ml, 6 N) was added in portions of 20 ml. The resulting mixture was then evaporated (60°, water bath) to a

volume of 10 ml and 2-propanol (300 ml) was added with stirring. 2-Propanol seems to dissolve everything except 1-methyluracil, which was obtained as a white precipitate. Recrystallization of the crude product from water (60 ml, 70°) gave 4.78 g (76%) of 1-methyluracil as a large, transparent crystals. Spectroscopic data (uv, ir, ¹H-nmr) of samples prepared this way were identical with those of authentic samples of 1-methyluracil obtained commercially.

Crystallography.

The X-ray data were collected on a Philips PW-1100 single crystal diffractometer using monochromated MoK α radiation ($\lambda = 0.71069 \text{ \AA}$) at -110° . A cylindrical crystal (diameter 0.6 mm, height 0.5 mm) was used for the measurements. The unit cell dimensions were calculated from 11 reflections ($10^\circ < \theta < 21^\circ$) centered on the diffractometer. Crystal and structure data are summarized in Table 3. Lp corrections were applied. The positions of the nonhydrogen atoms were obtained using the direct methods program XMY80 [8]. The nonhydrogen atoms were refined with anisotropic, the hydrogen atoms with isotropic thermal parameters. Final coordinates and temperature factors are given in Table 1. For the non-hydrogen atoms the equivalent isotropic parameters are listed. Table 2 gives bond distances and angles. Complex scattering factors for neutral atoms were taken from [9,10]. The SHELX-program package [11] was used for the calculations.

REFERENCES AND NOTES

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