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## Structure and Thermochemical Properties of Some Alkyluracils

BY KINGA SUWIŃSKA

*Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, PL-01 224 Warszawa, Poland*

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### Abstract

Crystalline 1,3,6-trisubstituted uracils have been analysed by X-ray diffraction. 1,3,6-Trimethyluracil,  $C_7H_{10}N_2O_2$  (I),  $M_r = 154.17$ , triclinic,  $P\bar{1}$ ,  $a = 7.242$  (2),  $b = 7.991$  (3),  $c = 8.380$  (3) Å,  $\alpha = 61.98$  (3),  $\beta = 63.40$  (3),  $\gamma = 82.09$  (3)°,  $V = 381.2$  (2) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.343$  Mg m<sup>-3</sup>,  $\lambda(Cu K\alpha) = 1.54178$  Å,  $\mu = 0.79$  mm<sup>-1</sup>,  $F(000) = 164$ , room temperature, final  $R = 0.060$  for 1216 observed reflections. 1,3-Dimethyl-6-ethyluracil,  $C_8H_{12}N_2O_2$  (II),  $M_r = 168.20$ , monoclinic,  $P2_1/n$ ,  $a = 4.107$  (1),  $b = 9.806$  (1),  $c = 20.994$  (2) Å,  $\beta = 92.97$  (1)°,  $V = 844.4$  (4) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.323$  Mg m<sup>-3</sup>,  $\lambda(Cu K\alpha) = 1.54178$  Å,  $\mu = 0.76$  mm<sup>-1</sup>,  $F(000) = 360$ , room temperature, final  $R = 0.049$  for 1284 observed reflections. 1,3-Dimethyl-6-propyluracil,  $C_9H_{14}N_2O_2$  (III),  $M_r = 182.22$ , monoclinic,  $P2_1/c$ ,  $a = 10.738$  (1),  $b = 11.735$  (1),  $c = 23.056$  (2) Å,  $\beta = 90.91$  (2)°,  $V = 2904.9$  (4) Å<sup>3</sup>,  $Z = 12$ ,  $D_x = 1.250$  Mg m<sup>-3</sup>,  $\lambda(Cu K\alpha) = 1.54178$  Å,  $\mu = 0.70$  mm<sup>-1</sup>,  $F(000) = 1176$ , room temperature, final  $R = 0.049$  for 3048 observed reflections. 1,3-Dimethyl-6-butyluracil,  $C_{10}H_{16}N_2O_2$  (IV),  $M_r = 196.25$ , monoclinic,  $P2_1/c$ ,  $a = 9.441$  (6),  $b = 12.086$  (4),  $c = 18.751$  (7) Å,  $\beta = 100.53$  (4)°,  $V = 2103$  (2) Å<sup>3</sup>,  $Z = 8$ ,  $D_x = 1.239$  Mg m<sup>-3</sup>,  $\lambda(Mo K\alpha) = 0.71073$  Å,  $\mu = 0.08$  mm<sup>-1</sup>,  $F(000) = 848$ , room temperature, final  $R = 0.063$  for 1812 observed reflections. In all structures, molecules are planar when only 'heavy' atoms are considered. A layered-type

structure was observed in all cases. In structures (III) and (IV), three and two independent molecules were found in the asymmetric unit, respectively. No conformational differences between the symmetrically non-equivalent molecules were detected. Correlations between thermochemical data and the properties of the compounds in the solid state are discussed.

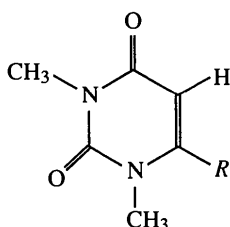
### Introduction

This investigation was undertaken as part of the thermochemical and structural studies of biologically significant nucleic acid bases and amino acids, which as part of the polynucleotide and polypeptide side chains are believed to be involved in the stereochemical control and recognition of substrates by those macromolecules. Methyl and other alkyl groups on pyrimidine and purine bases are known to play an important role in the formation of biologically active conformations of nucleic acids and contribute significantly to stacking interactions between both purine and pyrimidine bases in aqueous solutions. The number and position of attached alkyl groups determine the structure of their hydration shells and the character of the base–water interactions. The thermochemistry of aqueous solutions of alkylated pyrimidine bases was a subject of numerous investigations (Szemińska, Zielenkiewicz & Wierzchowski, 1979; Zielenkiewicz, Plesiewicz &

Table 1. Summary of data collection and structure refinement; Cu  $K\alpha$  X-rays were used for (I), (II) and (III) and Mo  $K\alpha$  for (IV)

	(I)	(II)	(III)	(IV)
Crystal size (mm)	0.21 × 0.24 × 0.60	0.11 × 0.32 × 0.39	0.14 × 0.25 × 0.42	0.21 × 0.28 × 0.35
Diffractometer	Enraf–Nonius CAD-4	Enraf–Nonius CAD-4	Enraf–Nonius CAD-4	Enraf–Nonius CAD-4
Lattice parameters (°)	31 < 2θ < 90	34 < 2θ < 72	26 < 2θ < 48	7 < 2θ < 21
Number of reflections	25	25	25	16
θ <sub>max</sub> (°)	70	70	70	25
Scan ranges				
<i>h</i>	0 → 8	0 → 5	0 → 12	0 → 11
<i>k</i>	−9 → 9	0 → 11	0 → 13	0 → 14
<i>l</i>	−8 → 10	−25 → 24	−24 → 25	−22 → 20
Measured reflections	1544	1917	4678	4014
Data with <i>I</i> > 2σ( <i>I</i> )	1434	1303	4289	3570
Unique observed reflections	1216	1284	3048	1812
<i>R</i> <sub>int</sub>	0.021	0.023	0.019	0.020
<i>R</i>	0.060	0.049	0.049	0.063
<i>wR</i>	0.063	0.051	0.051	0.049
<i>S</i>	5.65	3.28	3.19	2.57
Refined parameters	140	157	394	285
(Δ/σ) <sub>max</sub> in last cycle	0.01	0.02	0.01	0.03
Δρ (e Å <sup>−3</sup> )	−0.30; 0.22	−0.23; 0.23	−0.31; 0.25	−0.28; 0.25

Wierzchowski, 1979; Teplitsky, Yanson, Glukhova, Zielenkiewicz, Zielenkiewicz & Wierzchowski, 1980; Teplitsky, Glukhova, Sukhodub, Yanson, Zielenkiewicz, Zielenkiewicz, Kosiński & Wierzchowski, 1982; Grolier, Roux, Roux-Desgranges, Tomaszewicz & Zielenkiewicz, 1991; Zielenkiewicz, Zielenkiewicz & Wierzchowski, 1993, 1994). The values of enthalpies of solution, derived from experimentally determined enthalpies of sublimation and enthalpies of solution, measured for 1,3-dimethyluracils having different substituents at position 6 [methyl (I), ethyl (II), propyl (III) and butyl (IV); Zielenkiewicz, Zielenkiewicz & Wierzchowski, (1993)], revealed certain deviations from the linear approximation when the alkyl side chain at position 6 is regularly elongated. It seems reasonable to compare  $\Delta H_{\text{subl}}$  with the solid-state properties of these compounds, such as the density of the crystals, molar volume in the solid, packing coefficient or crystal packing energy, as well as details of molecular and crystal structure obtained by X-ray crystallography.

(I):  $R = \text{CH}_3$ (II):  $R = \text{C}_2\text{H}_5$ (III):  $R = \text{C}_3\text{H}_7$ (VI):  $R = \text{C}_4\text{H}_9$ 

In the present paper the crystal structures of the four 1,3-dimethyl-6-alkyluracils (I–IV) are reported and discussed in relation to their thermochemical properties.

### Experimental

Data collection was performed using an Enraf–Nonius CAD-4 diffractometer with a graphite monochromator

Table 2. Final atomic parameters ( $\times 10^4$ ), and equivalent isotropic displacement parameters ( $\text{\AA}^2$ ) for 1,3,6-trimethyluracil (I) (e.s.d.'s are given in parentheses)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
O(1)	3580 (2)	517 (2)	7021 (2)	0.0706 (7)
O(2)	8 (3)	4079 (2)	3455 (2)	0.0697 (8)
N(1)	331 (2)	−618 (2)	8070 (2)	0.0430 (6)
N(2)	1799 (2)	2322 (2)	5252 (2)	0.0459 (6)
C(1)	1983 (3)	735 (3)	6788 (3)	0.0454 (7)
C(2)	4 (3)	2654 (3)	4923 (3)	0.0466 (8)
C(3)	−1656 (3)	1219 (3)	6361 (3)	0.0457 (8)
C(4)	−1508 (3)	−359 (3)	7881 (3)	0.0415 (7)
C(5)	602 (3)	−2391 (3)	9629 (3)	0.0616 (10)
C(6)	3569 (4)	3768 (3)	3901 (4)	0.0700 (12)
C(7)	−3254 (3)	−1861 (3)	9381 (3)	0.0577 (7)

using the  $\omega$ –2θ scan technique. No absorption or secondary extinction correction was applied. Details of experimental conditions and structure refinement are summarized in Table 1.\* Three standard reflections were monitored every hour in each crystal; maximum variation 2%. Atomic scattering factors were from *International Tables for X-ray Crystallography* (1974, Vol. IV). All structures were solved by direct methods [*MULTAN*11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982)] and refined on *F* by full-matrix least squares with the *SDP* system (B. A. Frenz & Associates Inc., 1982). The H atoms were included in calculations with 'idealized' geometrical positions and were refined as 'riding' on their C atoms. [In the case of the ethyl derivative (II), the positional parameters of the H atoms were also refined.] Final refinement

\* List of structure factors, anisotropic thermal parameters, H-atom parameters and torsion angles have been deposited with the IUCr (Reference: NA0060). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Final atomic parameters ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2$ ) for 1,3-dimethyl-6-ethyluracil (II) (e.s.d.'s are given in parentheses)

$$U_{\text{eq}} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$U_{\text{eq}}$
O(1)	402 (3)	3785 (1)	1898 (1)	0.0650 (4)
O(2)	4972 (3)	2091 (2)	144 (1)	0.0728 (4)
N(1)	281 (3)	1488 (1)	1746 (1)	0.0441 (3)
N(2)	2653 (3)	2939 (1)	1015 (1)	0.0492 (4)
C(1)	1058 (4)	2797 (2)	1572 (1)	0.0465 (4)
C(2)	3499 (4)	1859 (2)	622 (1)	0.0500 (5)
C(3)	2519 (4)	533 (2)	829 (1)	0.0483 (4)
C(4)	986 (3)	359 (2)	1375 (1)	0.0414 (4)
C(5)	-1271 (4)	1334 (2)	2360 (1)	0.0577 (5)
C(6)	3511 (6)	4320 (2)	827 (1)	0.0702 (7)
C(7)	-3 (4)	-1006 (2)	1621 (1)	0.0492 (4)
C(8)	633 (5)	-2208 (2)	1194 (1)	0.0606 (9)

Table 4. Final atomic parameters ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2$ ) for 1,3-dimethyl-6-propyluracil (III) (e.s.d.'s are given in parentheses)

$$U_{\text{eq}} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$U_{\text{eq}}$
O(1A)	6050 (2)	788 (2)	739 (1)	0.0945 (7)
O(2A)	6577 (2)	4320 (2)	1489 (1)	0.0945 (8)
N(1A)	6158 (2)	959 (2)	1715 (1)	0.0624 (6)
N(2A)	6336 (2)	2551 (2)	1110 (1)	0.0630 (7)
C(1A)	6169 (2)	1392 (2)	1163 (1)	0.0644 (9)
C(2A)	6435 (2)	3302 (2)	1576 (1)	0.0660 (9)
C(3A)	6375 (2)	2773 (2)	2135 (1)	0.0636 (9)
C(4A)	6257 (2)	1646 (2)	2199 (1)	0.0580 (8)
C(5A)	6042 (3)	-289 (2)	1768 (1)	0.0940 (12)
C(6A)	6388 (3)	3021 (3)	520 (1)	0.0894 (12)
C(7A)	6242 (3)	1037 (2)	2775 (1)	0.0737 (9)
C(8A)	6244 (3)	1780 (2)	3295 (1)	0.0806 (11)
C(9A)	6245 (3)	1076 (3)	3855 (1)	0.0914 (12)
O(1B)	2719 (2)	-406 (1)	1804 (1)	0.0860 (7)
O(2B)	2747 (2)	3438 (1)	1988 (1)	0.0857 (7)
N(1B)	2890 (2)	653 (2)	982 (1)	0.0572 (7)
N(2B)	2774 (2)	1515 (2)	1899 (1)	0.0574 (6)
C(1B)	2789 (2)	531 (2)	1575 (1)	0.0603 (8)
C(2B)	2819 (2)	2604 (2)	1669 (1)	0.0606 (8)
C(3B)	2933 (2)	2652 (2)	1050 (1)	0.0597 (8)
C(4B)	2955 (2)	1714 (2)	720 (1)	0.0536 (7)
C(5B)	2948 (2)	-410 (2)	640 (1)	0.0835 (11)
C(6B)	2660 (3)	1402 (3)	2536 (1)	0.0820 (11)
C(7B)	3031 (2)	1740 (2)	70 (1)	0.0666 (8)
C(8B)	2975 (3)	2918 (2)	-201 (1)	0.0715 (9)
C(9B)	3082 (3)	2848 (3)	-860 (1)	0.0911 (12)
O(1C)	9421 (2)	3948 (2)	7158 (1)	0.0876 (7)
O(2C)	9657 (2)	3558 (2)	5206 (1)	0.1044 (8)
N(1C)	9643 (2)	2163 (2)	6791 (1)	0.0596 (7)
N(2C)	9554 (2)	3760 (2)	6183 (1)	0.0634 (7)
C(1C)	9528 (2)	3327 (2)	6738 (2)	0.0636 (8)
C(2C)	9651 (2)	3103 (2)	5680 (1)	0.0698 (10)
C(3C)	9751 (2)	1906 (2)	5779 (1)	0.0625 (8)
C(4C)	9761 (2)	1454 (2)	6313 (1)	0.0559 (8)
C(5C)	9626 (3)	1703 (2)	7386 (1)	0.0804 (10)
C(6C)	9465 (3)	5011 (2)	6118 (1)	0.0894 (12)
C(7C)	9918 (2)	204 (2)	6428 (1)	0.0684 (9)
C(8C)	10096 (3)	-540 (2)	5898 (1)	0.0771 (10)
C(9C)	10302 (3)	-1781 (2)	6067 (1)	0.0931 (12)

Table 5. Final atomic parameters ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2$ ) for 1,3-dimethyl-6-butyluracil (IV) (e.s.d.'s are given in parentheses)

$$U_{\text{eq}} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$U_{\text{eq}}$
O(1A)	7007 (3)	327 (2)	9661 (2)	0.0862 (12)
O(2A)	5881 (3)	3692 (2)	8639 (2)	0.0774 (12)
N(1A)	5207 (3)	419 (2)	8668 (2)	0.0556 (10)
N(2A)	6434 (3)	2013 (3)	9159 (2)	0.0545 (12)
C(1A)	6260 (4)	862 (3)	9183 (2)	0.0613 (16)
C(2A)	5645 (4)	2685 (3)	8627 (2)	0.0564 (16)
C(3A)	4571 (4)	2141 (3)	8113 (2)	0.0505 (14)
C(4A)	4351 (4)	1035 (3)	8137 (2)	0.0480 (13)
C(5A)	5020 (5)	-814 (3)	8720 (2)	0.0846 (20)
C(6A)	7512 (5)	2528 (3)	9724 (2)	0.0776 (20)
C(7A)	3226 (4)	433 (3)	7626 (2)	0.0537 (13)
C(8A)	2315 (4)	1120 (3)	7040 (2)	0.0528 (14)
C(9A)	1142 (4)	412 (3)	6585 (2)	0.0616 (16)
C(10A)	173 (4)	1051 (4)	5988 (2)	0.0740 (18)
O(1B)	-2186 (3)	-834 (2)	7710 (2)	0.0944 (14)
O(2B)	-2192 (3)	2765 (2)	7008 (2)	0.0782 (12)
N(1B)	-606 (3)	342 (2)	8386 (2)	0.0535 (12)
N(2B)	-2237 (3)	971 (3)	7372 (2)	0.0556 (12)
C(1B)	-1708 (4)	107 (3)	7814 (2)	0.0608 (15)
C(2B)	-1686 (4)	2058 (3)	7449 (2)	0.0572 (14)
C(3B)	-551 (4)	2209 (3)	8051 (2)	0.0544 (14)
C(4B)	-20 (4)	1398 (3)	8500 (2)	0.0482 (14)
C(5B)	-70 (5)	-613 (3)	8861 (2)	0.0783 (18)
C(6B)	-3401 (4)	750 (4)	6749 (2)	0.0771 (17)
C(7B)	1190 (4)	1543 (3)	9126 (2)	0.0544 (14)
C(8B)	1786 (4)	2712 (3)	9240 (2)	0.0567 (16)
C(9B)	3003 (4)	2764 (3)	9888 (2)	0.0623 (16)
C(10B)	3630 (5)	3930 (4)	10035 (2)	0.0840 (18)

## Results and discussion

### Structure (I)

The molecular structure and numbering scheme are illustrated in Fig. 1. The molecule is flat and the maximum deviation from the r.m.s. plane of 'heavy' atoms is 0.118 (2)  $\text{\AA}$  for the C(5) atom. The crystal packing shown in Fig. 2 reveals a layer-type structure. The layers are perpendicular to the *ab* diagonal of the unit cell, and the distance between the layers is 3.336 (3)  $\text{\AA}$ . All the intermolecular contacts are of van der Waals type; the intermolecular distances shorter than the sum of the van der Waals radii are: O(2)  $\cdots$  C(5<sup>i</sup>) 3.004 (2), C(2)  $\cdots$  C(4<sup>ii</sup>)

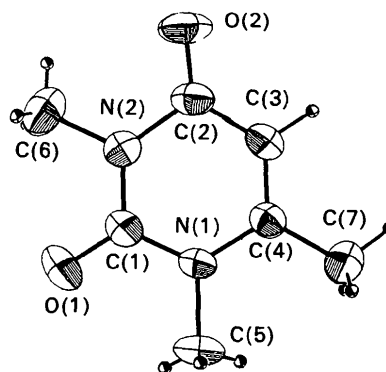


Fig. 1. The molecular structure of 1,3,6-trimethyluracil (I).

was performed using anisotropic thermal parameters (isotropic for H atoms);  $w = 1/\sigma^2(F_o)$ , where  $\sigma^2(F_o)$  is the e.s.d., based on counting statistics, of the observed structure factor. The final atom parameters are given in Tables 2–5.

3.358 (3) and  $O(1) \cdots H(3^{iii})$  2.45 Å [symmetry codes: (i)  $x, 1 + y, 1 - z$ ; (ii)  $-x, -y, 1 - z$ ; (iii)  $1 + x, y, z$ ].

### Structure (II)

The molecule including the atom numbering is shown in Fig. 3. The 'heavy' atoms of the molecule are planar and the maximum deviation from planarity is 0.069 (2) Å for C(5). Molecules are arranged in layers perpendicular to the  $2ac$  direction of the unit cell, with the interlayer distance 3.523 (2) Å (Fig. 4). Only the van der Waals packing forces occur in the crystal structure. The intermolecular distances shorter than the sum of van der Waals radii are:  $O(2) \cdots H(3^i)$  2.54 (2),  $C(7) \cdots H(51^{ii})$  2.90 (4) and  $H(61) \cdots H(81^{iii})$  2.38 (10) Å [symmetry codes: (i)  $1 - x, -y, -z$ ; (ii)  $-\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$ ; (iii)  $x, 1 + y, z$ ].

### Structure (III)

The asymmetric unit comprises three crystallographically independent 1,3-dimethyl-6-propyluracil molecules

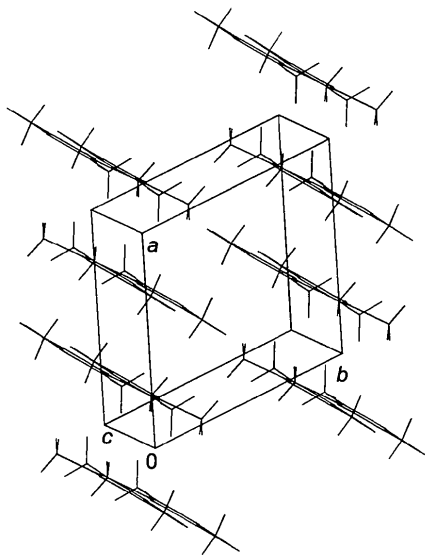


Fig. 2. Molecular packing in the crystal 1,3,6-trimethyluracil (I).

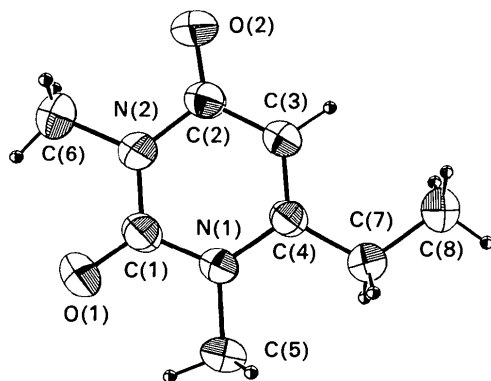


Fig. 3. The molecular structure of 1,3-dimethyl-6-ethyluracil (II).

(A, B and C); the atom numbering scheme is displayed in Fig. 5. There are no significant conformational differences between these three molecules, therefore, only one is shown in the ORTEP II (Johnson, 1976) drawing. The molecules are planar and the maximum deviations of atoms from planarity are: 0.071 (3) for C(8A) (molecule A), 0.077 (3) for C(8B) (molecule B) and 0.097 (3) Å for C(9C) (molecule C). The structure is of a layer-type with the layers perpendicular to the crystallographic  $a$ -axis (Fig. 6). Two types of layer occur in the crystal structure: layer C (at  $x =$

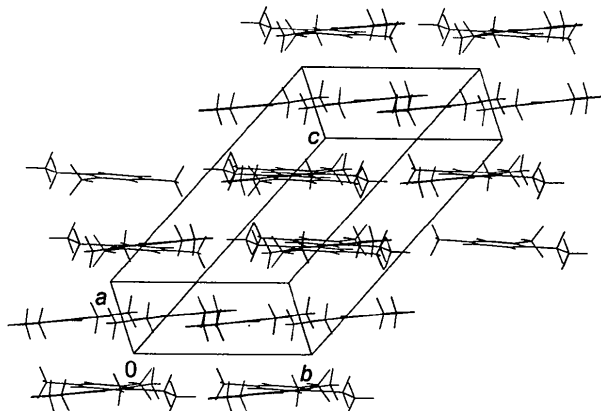


Fig. 4. Molecular packing in the crystal 1,3-dimethyl-6-ethyluracil (II).

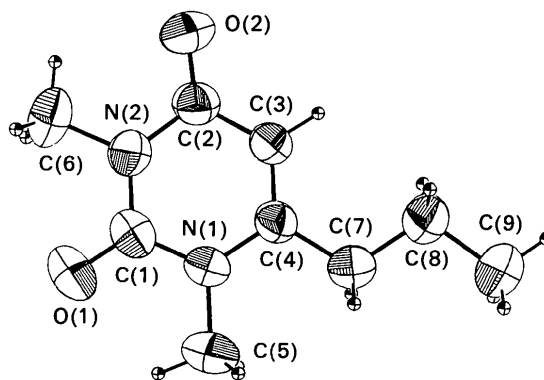


Fig. 5. The molecular structure of 1,3-dimethyl-6-propyluracil (III).

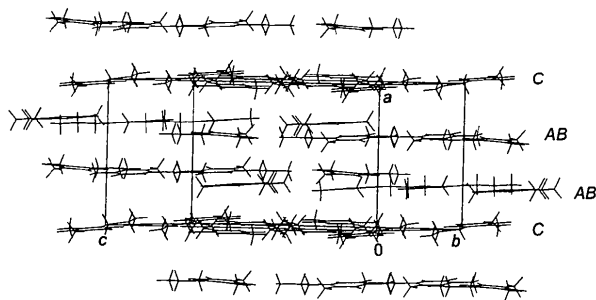


Fig. 6. Molecular packing in the crystal 1,3-dimethyl-6-propyluracil (III).

0) built out of molecules *C* and layer *AB* (at  $x = \frac{1}{3}$  and  $\frac{2}{3}$ ) composed of molecules *A* and *B*. In Fig. 7 the arrangement of molecules in both layers is illustrated. In the layer (*AB*) molecules *A* and *B* are arranged in two 'sublayers' separated by approximately 0.96 Å. The

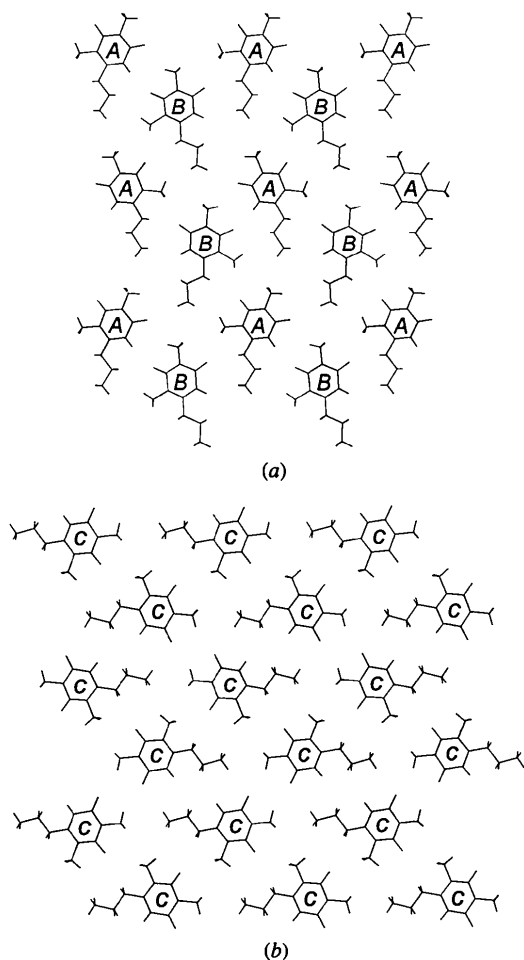


Fig. 7. Arrangement of the 1,3-dimethyl-6-propyluracil (III) in (a) layer *AB* and (b) layer *C*.

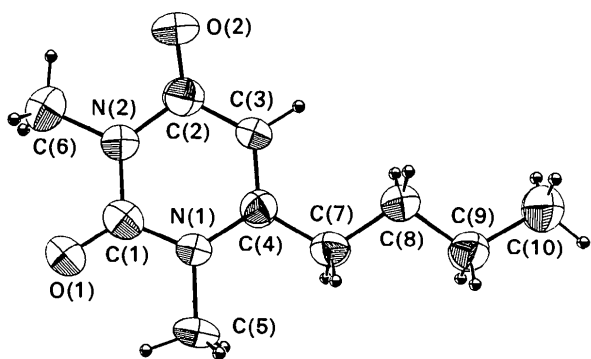


Fig. 8. The molecular structure of 1,3-dimethyl-6-butyluracil (IV).

sequence of layers is *C(BA)(AB)C* and the interlayer distances are: 3.098 (2) and 3.675 (2) Å for layers *C*···(*BA*) and (*BA*)···(*AB*), respectively. Intermolecular forces are of the van der Waals type only. The intermolecular distances shorter than the sum of the van der Waals radii are: O(1*B*)···H(3*A*<sup>i</sup>) 2.48 and H(93*B*)···H(93*C*<sup>ii</sup>) 2.32 Å [symmetry codes: (i)  $1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$ ; (ii)  $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$ ].

#### Structure (IV)

The crystals are composed of two independent 1,3-dimethyl-6-butyluracil molecules, *A* and *B*. In Fig. 8 the molecular structure including the atom numbering is shown. As no significant conformational differences between the two molecules were detected, only one

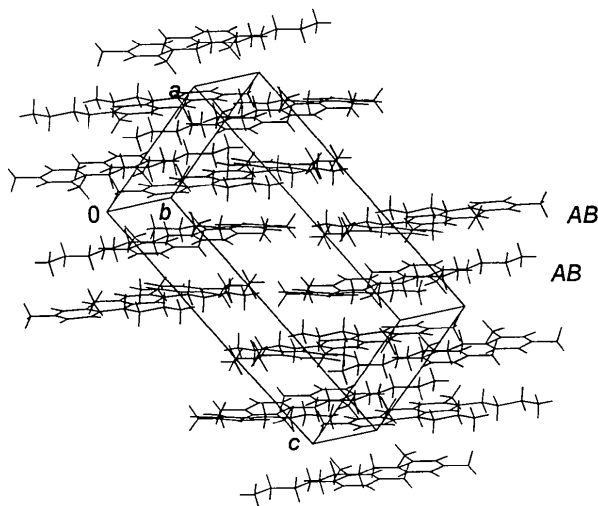


Fig. 9. Molecular packing in the crystal 1,3-dimethyl-6-butyluracil (IV).

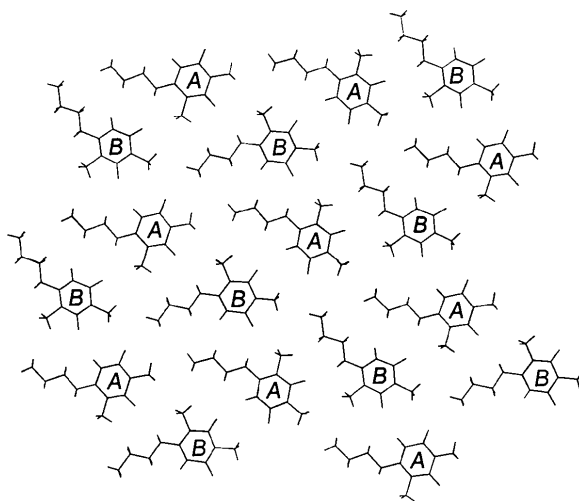


Fig. 10. Arrangement of the 1,3-dimethyl-6-butyluracil (IV) molecules in the layer.

Table 6. Bond distances ( $\text{\AA}^2$ ) for non-H atoms (*e.s.d.*'s are given in parentheses)

	(I)	(II)	(III <sub>A</sub> )	(III <sub>B</sub> )	(III <sub>C</sub> )	(IV <sub>A</sub> )	(IV <sub>B</sub> )
O(1)—C(1)	1.233 (3)	1.224 (2)	1.212 (3)	1.221 (3)	1.220 (3)	1.220 (5)	1.226 (5)
O(2)—C(2)	1.221 (2)	1.220 (2)	1.221 (3)	1.228 (3)	1.216 (3)	1.236 (5)	1.224 (5)
N(1)—C(1)	1.367 (2)	1.377 (2)	1.371 (3)	1.382 (2)	1.377 (3)	1.362 (5)	1.380 (5)
N(1)—C(4)	1.388 (3)	1.394 (2)	1.380 (3)	1.385 (3)	1.388 (3)	1.379 (4)	1.391 (5)
N(1)—C(5)	1.472 (3)	1.474 (2)	1.474 (3)	1.477 (3)	1.476 (3)	1.506 (5)	1.488 (5)
N(2)—C(1)	1.362 (2)	1.377 (2)	1.378 (3)	1.376 (3)	1.378 (3)	1.402 (5)	1.370 (5)
N(2)—C(2)	1.413 (3)	1.397 (2)	1.392 (3)	1.385 (3)	1.397 (3)	1.393 (5)	1.411 (5)
N(2)—C(6)	1.462 (3)	1.458 (3)	1.471 (3)	1.480 (3)	1.478 (3)	1.467 (5)	1.475 (5)
C(2)—C(3)	1.413 (2)	1.435 (2)	1.433 (3)	1.436 (3)	1.426 (4)	1.426 (5)	1.418 (5)
C(3)—C(4)	1.341 (2)	1.347 (2)	1.337 (3)	1.339 (3)	1.338 (3)	1.356 (5)	1.329 (5)
C(4)—C(7)	1.482 (3)	1.498 (2)	1.508 (3)	1.503 (3)	1.500 (3)	1.485 (5)	1.491 (5)
C(7)—C(8)	—	1.511 (3)	1.483 (3)	1.519 (4)	1.517 (3)	1.514 (5)	1.522 (5)
C(8)—C(9)	—	—	1.532 (4)	1.527 (3)	1.523 (4)	1.530 (5)	1.513 (5)
C(9)—C(10)	—	—	—	—	—	1.521 (5)	1.534 (6)

Table 7. Bond angles ( $^\circ$ ) for non-H atoms (*e.s.d.*'s are given in parentheses)

	(I)	(II)	(III <sub>A</sub> )	(III <sub>B</sub> )	(III <sub>C</sub> )	(IV <sub>A</sub> )	(IV <sub>B</sub> )
C(4)—N(1)—C(5)	121.2 (2)	121.3 (1)	121.2 (2)	121.6 (2)	121.5 (2)	121.3 (3)	122.5 (3)
C(1)—N(1)—C(5)	117.2 (2)	116.4 (1)	116.6 (2)	116.5 (2)	116.3 (2)	114.9 (3)	115.5 (3)
C(1)—N(1)—C(4)	121.6 (2)	122.3 (1)	122.2 (2)	121.9 (2)	122.2 (2)	123.7 (3)	122.0 (3)
C(2)—N(2)—C(6)	118.9 (2)	118.2 (1)	118.2 (2)	117.9 (2)	118.1 (2)	118.6 (3)	117.2 (3)
C(1)—N(2)—C(6)	117.2 (2)	117.1 (1)	117.3 (2)	117.7 (2)	117.3 (2)	117.9 (3)	118.5 (3)
C(1)—N(2)—C(2)	123.9 (2)	124.6 (1)	124.5 (2)	124.4 (2)	124.7 (2)	123.5 (3)	124.2 (3)
N(1)—C(1)—N(2)	117.6 (2)	116.6 (1)	116.8 (2)	116.9 (2)	116.4 (2)	116.2 (3)	116.9 (3)
O(1)—C(1)—N(2)	121.5 (2)	121.5 (2)	121.3 (2)	121.3 (2)	121.5 (2)	119.6 (3)	121.9 (4)
O(1)—C(1)—N(1)	120.8 (2)	121.9 (2)	121.9 (2)	121.7 (2)	122.1 (2)	124.2 (4)	121.2 (4)
O(2)—C(2)—N(2)	119.5 (2)	119.5 (2)	120.1 (2)	120.2 (2)	120.3 (2)	119.4 (3)	119.3 (3)
N(2)—C(2)—C(3)	114.7 (2)	115.3 (1)	114.5 (2)	115.0 (2)	114.7 (2)	115.9 (3)	114.3 (3)
O(2)—C(2)—C(3)	125.8 (2)	125.2 (2)	125.4 (2)	124.8 (2)	125.1 (2)	124.7 (4)	126.4 (4)
C(2)—C(3)—C(4)	122.4 (2)	121.5 (2)	122.3 (2)	122.3 (2)	122.4 (2)	121.8 (3)	123.5 (3)
N(1)—C(4)—C(3)	119.7 (2)	119.7 (1)	119.6 (2)	119.5 (2)	119.5 (2)	118.9 (3)	119.1 (3)
C(3)—C(4)—C(7)	122.1 (2)	123.6 (1)	124.6 (2)	123.4 (2)	123.3 (2)	123.9 (3)	123.9 (3)
N(1)—C(4)—C(7)	118.2 (2)	116.7 (1)	115.7 (2)	117.1 (2)	117.1 (2)	117.3 (3)	117.0 (3)
C(4)—C(7)—C(8)	—	115.7 (1)	115.8 (2)	115.3 (2)	115.8 (2)	116.4 (3)	115.5 (3)
C(7)—C(8)—C(9)	—	—	111.4 (2)	111.0 (2)	111.3 (2)	110.8 (3)	111.0 (3)
C(8)—C(9)—C(10)	—	—	—	—	—	113.7 (3)	113.1 (3)

molecule is plotted in the *ORTEP*II (Johnson, 1976) diagram. The molecules are planar with maximum deviations from planarity 0.102 (3) for C(6A) (molecule A) and 0.030 (3)  $\text{\AA}$  for atom N(2B) (molecule B). As found for the other structures, the structure here is also of the layer-type, with layers perpendicular to the *ac* diagonal of the unit cell (Fig. 9). In Fig. 10 the arrangement of molecules A and B in one layer is represented. Molecules A and B form two 'sublayers' separated by approximately 0.56  $\text{\AA}$  and the sequence of layers is (AB)(BA)(AB). The interlayer distances are: 3.743 (1) and 3.516 (1)  $\text{\AA}$  for layers (BA)  $\cdots$  (AB) and (AB)  $\cdots$  (BA), respectively. Only van der Waals intermolecular interactions exist between the 1,3-dimethyl-6-butyluracil molecules. The intermolecular distances shorter than the sum of the van der Waals radii are: C(4A)  $\cdots$  H(63B<sup>i</sup>) 2.89 and H(62B)  $\cdots$  H(102B<sup>ii</sup>) 2.31  $\text{\AA}$  [symmetry codes: (i)  $1 + x, y, z$ ; (ii)  $-x, -\frac{1}{2} + y, \frac{3}{2} - z$ ].

Bond lengths and angles for structures (I)–(IV) are collected in Tables 6 and 7. In crystals (III) and (IV) more than one molecule occurs in the asymmetric unit; three in (III) and two in (IV). Comparison of the bond distances and valence angles obtained here with those observed in other known structures of uracil (Stewart

& Jensen, 1967) and uracils substituted with methyl group(s) in different positions (Banerjee, Dattagupta, Saenger & Rabczenko, 1977; Khomenko, Mitkeyich & Sukhodub, 1986; Ozeki, Sakabe & Tanaka, 1969; Gardil, 1961) show no significant differences in geometry and do not merit comment. The molecules in all four structures are planar, including the aliphatic substituents which assume the energetically most favourable *trans* conformation around all the  $Csp^3-Csp^3$  bonds; C(8) is always *trans* to the N(1)—C(4) endocyclic bond of the diketopyrimidine ring.

#### Crystal packing energies and enthalpies of sublimation

The experimental enthalpies of sublimation  $\Delta H_{\text{subl}}$  (Table 8) do not change linearly with the elongation of 1,3-dimethyl-6-alkyluracils by the addition of successive  $-\text{CH}_2-$  groups from methyl to butyl (Zielenkiewicz, Zielenkiewicz & Wierzchowski, 1993). Substitution of the H atom in position 6 by a  $\text{CH}_3-$  group, *i.e.* change from 1,3-dimethyluracil to 1,3,6-trimethyluracil (I), reflects in  $\Delta H_{\text{subl}}$  by a gain of 25.0  $\text{kJ mol}^{-1}$ , while the elongation to ethyl (II) reflects in a loss in  $\Delta H_{\text{subl}}$ . Subsequent elongation to the odd three-membered propyl chain in (III) increases  $\Delta H_{\text{subl}}$ , and again for

Table 8. *Thermochemical and crystal packing data*

Compound	$\Delta H_{\text{subl}}$ (kJ mol <sup>-1</sup> )	$V_{\text{mol}}$ (m <sup>3</sup> × 10 <sup>-6</sup> )	$\Delta V_{\text{mol}}$ (m <sup>3</sup> × 10 <sup>-6</sup> )	$D_x$ (Mg m <sup>-3</sup> )	Packing coefficient	Packing energy (kJ mol <sup>-1</sup> )
1,3-DM-U*	86.7 (0.7)	99.2		1.412	0.73	121.3
(I)	111.7 (1.0)	114.8	15.4	1.343	0.72	127.6
(II)	96.1 (1.1)	127.3	12.5	1.323	0.73	158.6
(III)	109.2 (1.2)	145.8	18.0	1.250	0.71	97.5
(IV)	90.6 (1.4)	158.1	12.3	1.247	0.72	111.3

\* 1,3-Dimethyluracil; crystal data from Banerjee, Dattagupta, Saenger & Rabczenko (1977).

the four-membered butyl chain a decrease of  $\Delta H_{\text{subl}}$  is observed. Irregularities are also observed in the crystal density  $D_x$ , where transformation of 1,2-dimethyluracil into (I) results in decreasing  $D_x$  by approximately 0.07 Mg m<sup>-3</sup>. Addition of the next —CH<sub>2</sub>— group does not significantly influence the crystal density, but increasing the length of the side chain by the third —CH<sub>2</sub>— group reveals a similar effect to the first addition, *i.e.* a decrease in the  $D_x$  value by *ca* 0.07 Mg m<sup>-3</sup>. It seems that the elongation of the side chain by an odd number of —CH<sub>2</sub>— groups causes a decrease in  $D_x$ , while the addition of the next and achieving an even number of —CH<sub>2</sub>— groups leaves the  $D_x$  value practically unchanged. Again, the molar volume (in the solid state) changes in a similar way to  $\Delta H_{\text{subl}}$ : the increase in molar volume is larger when the number of —CH<sub>2</sub>— groups changes from even to odd than for the elongation from odd to even. From the above, the following conclusion can be assumed: effects caused by regular elongation at position 6 in 1,3-dimethyluracil are different when the addition ends with an odd- or even-membered *n*-alkyl chain. Achieving an odd number of —CH<sub>2</sub>— groups results in higher  $\Delta H_{\text{subl}}$  and larger  $\Delta V_{\text{mol}}$  values with a parallel decrease in crystal density; achieving an even number of —CH<sub>2</sub>— groups results in a decrease in  $\Delta H_{\text{subl}}$ , the increase in molar volume is smaller and the crystal density remains the same as for the (*n* - 1)-member neighbour. It is important to notice that the crystal packing coefficients for 1,3-dimethyluracil and the four structures reported herein are very similar, ranging from 0.71 to 0.73. For comparison with experimental enthalpies of sublimation, the crystal packing energies were calculated using the non-bonded atom-atom potentials

$$E_{ij} = A \exp(-BR_{ij})R^{-D} - CR^{-6},$$

which is a mixed potential of Lenard-Jones and Buckingham type. *A*, *B*, *C* and *D* are empirical parameters established for each atom-atom interaction (Giglio, 1968), the double index designated any pair of atoms in different molecules at a distance of  $R_{ij}$ , and the total packing energy is a lattice sum over *i* and *j*. Comparison

of the calculated packing energies with experimental sublimation enthalpies shows some discrepancies, which are particularly large for 1,3-dimethyl-6-ethyluracil.

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