of 111.0 (4) and 125.3 (5)° respectively. The crystal packing is governed by van der Waals interactions.

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Structures of 6-Amino-1,3-dimethyl-5-nitrosouracil Monohydrate and 6-Amino-5-formyl-1,3-dimethyluracil Monohydrate

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Abstract. 6-Amino-1,3-dimethyl-5-nitroso-2,4(1*H*,3*H*)-pyrimidinedione monohydrate (DANU), $C_6H_8N_4O_2.H_2O$, $M_r = 202.17$, orthorhombic, *Pnam*, $a = 13.978\ (10)$, $b = 9.638\ (8)$, $c = 6.338\ (11)$ Å, $V = 853.9$ Å^3, $Z = 4$, $D_x = 1.57$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 0.88$ cm^{-1}, $F(000) = 424$, $T = 293$ K, $R = 0.043$ for 709 unique observed reflections [$F_o > 6\sigma(F)$]. 6-Amino-5-formyl-1,3-dimethyl-2,4(1*H*,3*H*)-pyrimidinedione monohydrate (DAFU), $C_7H_9N_3O_2.H_2O$, $M_r = 201.18$, monoclinic, $C2/c$, $a = 15.557\ (11)$, $b = 7.562\ (11)$, $c = 16.972\ (13)$ Å, $\beta = 116.69\ (5)°$, $V = 1783.88$ Å^3, $Z = 8$, $D_x = 1.50$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 0.81$ cm^{-1}, $F(000) = 848$, $T = 293$ K, $R = 0.056$ for 718 unique observed reflections [$F_o > 6\sigma(F)$]. The molecular structures of the free uracil derivatives investigated are similar to those found for similar derivatives of uracil whose structures have been determined as ligands in various metal complexes.

Introduction. This investigation is part of a series of structural studies of pyrimidine derivatives, in this case with amino substituents on C6. The aim of these studies is to elucidate the role that metal–pyrimidine complexes play in biological systems. To date the structures of several metal complexes (Moreno, Salas, Colacio, Sánchez & Nieto, 1986; Romero, Moreno, Ruiz, Sánchez & Nieto, 1986; Romero-Molina, Gutiérrez-Valero, López-Garzón, Salas-Peregrín, Arriortúa-Marcaida & Zuñiga, 1987; García-Megías, Colacio-Rodríguez, García-Rodríguez, Salas-Peregrín, Simard & Beauchamp, 1989; Kivekäs, Colacio, Ruiz, López-González & León, 1989; Suárez-Varela, Legros, Galy, Colacio-

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Rodríguez, Ruiz, López-González, León & Perona, 1989) have been determined. In this paper we report the structures of two uncomplexed uracil derivatives.

Experimental. *DANU.* Deep-purple crystals were obtained from aqueous solution. Data were collected on a Nicolet *P*3 (four-circle) diffractometer. The crystal had dimensions $0.16 \times 0.38 \times 0.4$ mm. Cell parameters were measured on the diffractometer using 14 reflections in the 2θ range 17–23°. Range of indices: $0 \le h \le 20$; $0 \le k \le 14$; $0 \le l \le 10$. Data measured using $\omega/2\theta$ scans in the range $0 < 2\theta < 60°$. Intensities of standard reflections, 126 and 150, measured every 50 reflections, did not vary by more than 2% of their mean values throughout the data collection. Lorentz and polarization factors were applied. No corrections for absorption or secondary extinction were made. 1483 independent reflections measured, 709 observed [$F_o > 6\sigma(F)$] reflections were used in the refinement. The structure was solved using the *SHELXS*86 program (Sheldrick, 1985). The *E* map revealed the positions of all non-H atoms.

A difference synthesis revealed the positions of all H atoms. All H atoms were kept fixed in these positions and were given fixed isotropic temperature factors: $U(\mathrm{H}) = 0.05$ Å^2, approximately 1.5 times the U_{eq} value of the parent atom. All other atoms were refined anisotropically. Full-matrix refinement (on *F*) using the program *SHELX*76 (Sheldrick, 1976) converged at $R = 0.043$, $wR = 0.037$; unit weights; 85 refined parameters; max. shift/e.s.d. < 0.001; max. $\Delta\rho = 0.39$, min. $= -0.26$ e Å^{-3}.

Structure solution and refinement was first carried out in $Pna2_1$; the absences were also consistent with *Pnam* but this possibility was discounted initally since it required the molecule to lie on a mirror plane. Difficulty was experienced with the $Pna2_1$ refinement. Although the value of *R* fell to 0.040, this was only achieved by applying a damping factor in the least-squares refinement, otherwise quite large oscillations occurred in the values of shift/e.s.d. Undamped, the *R* factor stood at 0.042. The refinement was then repeated in *Pnam* with all non-H atoms lying on the mirror plane at $z = 0.25$. This model converged to $R = 0.043$ within six cycles. It was decided that *Pnam* was the more satisfactory representation of the structure.

DAFU. Experimental methods as for DANU unless stated otherwise. Yellow crystals were obtained from aqueous solution. The crystal had dimensions $0.04 \times 0.5 \times 0.5$ mm. Cell parameters using 14 reflections in the 2θ range 12–21°. Range of indices: $0 \le h \le 20$; $0 \le k \le 10$; $-22 \le l \le 22$. Data measured using $\omega/2\theta$ scans in the range $0 < 2\theta < 50°$. Intensities of standard reflections, $22\bar{2}$ and 206, measured every 50 reflections, did not vary by more than 2% of their mean values throughout the data collection. 1774 independent reflections measured, 718 observed [$F_o > 6\sigma(F)$] reflections were used in the refinement. The structure was solved using the *SHELXS*86 program (Sheldrick, 1985).

The methyl H atoms and that on C51 were put in calculated positions. Those on N6 and O*W*1 were revealed in a difference synthesis. All H atoms were then allowed to ride on their parent atoms and given fixed isotropic temperature factors approximately 1.5 times the U_{eq} value of the parent atom. All other

Table 1. *Coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* (Å$^2 \times 10^3$) *for non-*H *atoms with e.s.d.'s in parentheses*

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

	x	*y*	*z*	U_{eq}
DANU				
N1	6983 (2)	592 (3)	2500*	28 (1)
C1	6178 (3)	1575 (4)	2500*	38 (1)
C2	7909 (3)	1147 (4)	2500*	31 (1)
O2	8030 (2)	2394 (3)	2500*	42 (1)
N3	8657 (2)	229 (3)	2500*	30 (1)
C3	9618 (2)	853 (4)	2500*	41 (1)
C4	8567 (2)	−1216 (3)	2500*	28 (1)
O4	9280 (2)	−1948 (3)	2500*	42 (1)
C5	7593 (2)	−1737 (4)	2500*	26 (1)
N5	7534 (2)	−3127 (3)	2500*	34 (1)
O5	6707 (2)	−3700 (3)	2500*	43 (1)
C6	6801 (2)	−796 (3)	2500*	26 (1)
N6	5925 (2)	−1249 (3)	2500*	34 (1)
O*W*1	4113 (2)	78 (3)	2500*	47 (1)
DAFU				
N1	8079 (3)	1624 (7)	3990 (3)	38 (1)
C1	8287 (5)	2566 (11)	3330 (4)	51 (2)
C2	8834 (4)	1431 (10)	4816 (4)	42 (2)
O2	9620 (3)	2026 (7)	5002 (3)	56 (1)
N3	8638 (3)	529 (7)	5429 (3)	39 (1)
C3	9448 (5)	310 (11)	6313 (4)	54 (2)
C4	7734 (4)	−105 (9)	5285 (4)	40 (2)
O4	7654 (3)	−773 (7)	5891 (3)	33 (1)
C5	6994 (4)	132 (2)	4398 (4)	38 (2)
C51	6054 (5)	−511 (10)	4201 (5)	54 (2)
O5	5341 (3)	−419 (8)	3491 (3)	69 (2)
C6	7185 (4)	945 (9)	3764 (4)	36 (2)
N6	6534 (3)	1065 (8)	2932 (3)	44 (1)
O*W*1	6493 (3)	2701 (7)	1403 (3)	53 (1)

* Coordinate is fixed, atoms lie on mirror plane.

Table 2. *Interatomic distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

X = N5 (DANU) and C51 (DAFU).

	DANU	DAFU		DANU	DAFU
C1—N1	1.471 (4)	1.482 (8)	C2—N1	1.400 (4)	1.374 (7)
C6—N1	1.361 (4)	1.365 (7)	O2—C2	1.214 (4)	1.205 (7)
N3—C2	1.370 (4)	1.386 (8)	C3—N3	1.472 (4)	1.473 (7)
C4—N3	1.398 (4)	1.399 (8)	O4—C4	1.220 (4)	1.202 (7)
C5—C4	1.452 (4)	1.438 (8)	*X*—C5	1.342 (5)	1.430 (9)
C6—C5	1·431 (5)	1.382 (8)	O5—*X*	1.281 (4)	1.219 (8)
N6—C6	1·300 (4)	1.321 (7)			
C2—N1—C1	117.4 (3)	116.5 (5)	C6—N1—C1	119.3 (3)	120.6 (5)
C6—N1—C2	123.2 (3)	122.9 (6)	O2—C2—N1	120.5 (4)	122.0 (6)
N3—C2—N1	117.3 (3)	116.2 (6)	N3—C2—O2	122.2 (3)	121.8 (6)
C3—N3—C2	115.7 (3)	116.3 (5)	C4—N3—C2	125.1 (3)	125.5 (5)
C4—N3—C3	119.2 (3)	118.1 (6)	O4—C4—N3	120.2 (3)	118.5 (5)
C5—C4—N3	115.4 (3)	114.2 (6)	C5—C4—O4	124.4 (3)	127.3 (6)
X—C5—C4	113.7 (3)	117.1 (6)	C6—C5—C4	120.4 (3)	121.3 (6)
C6—C5—*X*	125.8 (3)	121.6 (6)	O5—*X*—C5	119.1 (3)	126.3 (7)
C5—C6—N1	118.5 (3)	119.8 (6)	N6—C6—N1	120.4 (3)	118.0 (6)
N6—C6—C5	121.0 (3)	122.2 (6)			

atoms were refined anisotropically. Full-matrix refinement (on F) using the program *SHELX*76 (Sheldrick, 1976) converged at $R = 0.056$, $wR = 0.057$; unit weights; 133 refined parameters; max. shift/e.s.d. < 0.002; max. $\Delta\rho = 0.34$, min. = -0.21 e Å^{-3}.

Scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). The program packages *XANADU* (Roberts & Sheldrick, 1975), *SHELX*76 (Sheldrick, 1976), *PLUTO* (Motherwell & Clegg, 1978), and *SHELXS*86 (Sheldrick, 1985) were also used. All calculations were carried out on the Dundee University PRIME computer.

Discussion. The final coordinates are shown in Table 1 and the bond lengths and angles are given in Table 2.* The atomic numbering is shown in Fig. 1.

The bond lengths, according to data reported by Ladd (1979), indicate that in both compounds extensive electronic delocalization exists in the pyrimidine ring. Only the exocyclic C=O bonds appear to be true double bonds, whereas the formally single C6—N6 bonds exhibit a pronounced double-bond character which is in accord with the chemical behaviour of these 6-amino groups. In the same way, both 5-nitroso and 5-formyl groups would be represented as a resonance hybrid of the two canonical forms $—X{=}O \leftrightarrow {=}X—O$.

The hydrogen-bonding scheme is given in Table 3. In both structures one of the amino H atoms forms a bond between N6 and O*W*1 and the other is involved in a short intramolecular contact with O5, *i.e.* the nitroso or formyl O atom. This latter contact explains the appearance of one signal for the resonance of each amino proton in the ^{1}H NMR spectra of these compounds.

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54443 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

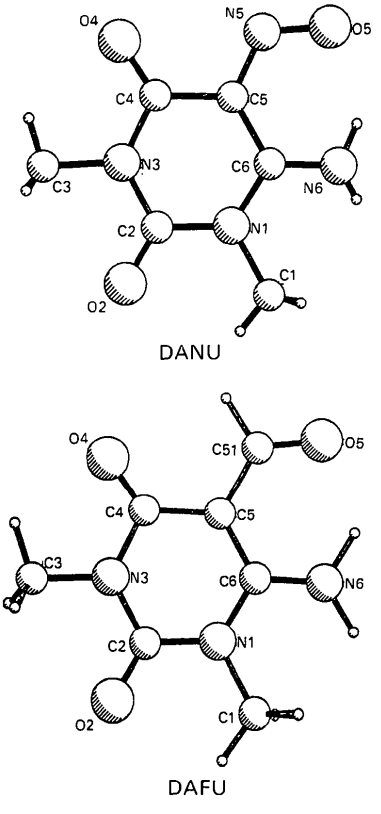

Fig. 1. Perspective views of the molecules showing atomic numbering.

Table 3. *Hydrogen-bonding geometry* (Å, °)

A—H···*B*		*A*—H	H···*B*	*A*···*B*	*A*—H···*B*
DANU					
O*W*1—H1*W*1···O2	(*a*)	0.88	2.00	2.86 (1)	170 (1)
O*W*1—H2*W*1···N5	(*b*)	0.73	2.20	2.90 (1)	160 (1)
N6—H1N6···O*W*1	(*c*)	0.85	1.89	2.60 (1)	141 (1)
N6—H2N6···O5	(*c*)	0.70	2.16	2.84 (1)	162 (1)

Symmetry code: (*a*) $-0.5 + x$, $-1.5 - y$, $0.5 - z$; (*b*) $-0.5 + x$, $-0.5 - y$, $0.5 - z$; (*c*) x, y, z.

DAFU					
O*W*1—HO*W*1···O2	(*a*)	0.99	1.76	2.75 (1)	179 (1)
O*W*1—HO*W*2···O4	(*b*)	1.02	1.80	2.82 (1)	179 (1)
N6—H1N6···O5	(*c*)	1.08	1.85	2.68 (1)	129 (1)
N6—H2N6···O*W*1	(*c*)	1.09	1.81	2.85 (1)	159 (1)

Symmetry code: (*a*) $x - 0.5$, $0.5 - y$, $z - 0.5$; (*b*) x, $-y$, $z - 0.5$; (*c*) x, y, z.

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