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Intermolecular N—H···O=C Hydrogen-Bonding in the Crystal Structure of 6-Amino-1,3-dimethyluracil

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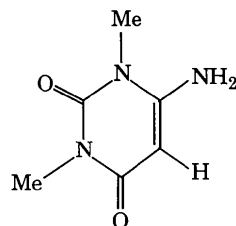
Abstract

The 6-amino-1,3-dimethyluracil molecule [6-amino-1,3-dimethyl-2,4(1*H*,3*H*)-pyrimidinedione], $C_6H_9N_3O_2$ (I), lies on a crystallographic mirror plane and participates in an extensive two-dimensional hydrogen-bonding network in the solid state. Each molecule is involved in N—H···O=C hydrogen bonding involving the amino and carbonyl groups, with O···N separations of 2.894 (3) and 2.904 (3) Å.

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Comment

Hydrogen bonds often provide the strongest intermolecular forces between molecules in organic molecular crystals and hence often dictate the preferred packing arrangement. The general principles underlying hydrogen-bond formation are reasonably well understood and the structures of hydrogen-bonded crystals can often be rationalized in terms of the preferred combinations of hydrogen-bond donors and acceptors (Etter, 1990; Etter, McDonald & Bernstein, 1990; Etter & Reutzel, 1991). In general, the strongest hydrogen-bond donors pair off with the strongest hydrogen-bond acceptors. Similar pairing processes are repeated until all the hydrogen-bond donors and acceptors have been utilized. Herein we report the formation of a two-dimensional network of intermolecular N—H···O=C hydrogen bonds in the structure of 6-amino-1,3-dimethyluracil (I).

The 6-amino-1,3-dimethyluracil molecule (I) lies on a crystallographic mirror plane and participates in an extensive two-dimensional hydrogen-bonding network in the solid state (see Fig. 1). The bond lengths in this structure are similar to those previously observed in related structures, *e.g.* C=O 1.224 (3) and 1.237 (3) Å; C(sp^3)—N 1.460 (3) and 1.458 (3) Å. Likewise, the bond angles do not deviate from the accepted values and are in the range 115.8 (2) for N(3)—C(4)—C(5) to 125.5 (2)° for O(4)—
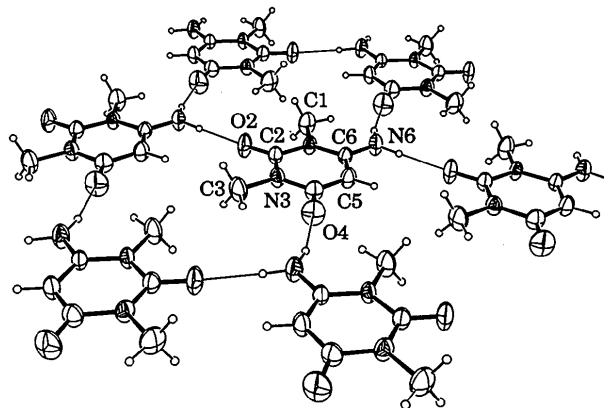

Fig. 1. A view of the two-dimensional hydrogen-bonding environment in the crystal structure of 6-amino-1,3-dimethyluracil (I). The non-H atoms are depicted with thermal ellipsoids drawn at the 50% probability level. For clarity the H atoms are drawn as small spheres of an arbitrary size.

C(4)—C(5). As the molecule lies on a mirror plane, all the torsion angles involving non-H atoms are either 0 or 180°.

There have been many structural determinations of uracil derivatives reported, both as organic structures and metal-complex derivatives. A search of the January 1992 release of the Cambridge Structural Database (Allen, Kennard & Taylor, 1983) reveals that the most closely related structural determinations to the present study include: (i) 6-amino-5-cinnamoyl-1,3-dimethyluracil (Warin, Foulon, Baert, Bernier & Henichart, 1980); (ii) 5-cinnamoyl-1,3-dimethyl-6-[(2-morpholinoethyl)amino]-uracil hydrochloride (Warin, Baert, Bernier & Henichart, 1984); (iii) 6-[cinnamoyl(2-morpholinoethyl)amino]-1,3-dimethyluracil (Warin, Lobry, Bernier & Henichart, 1984); and (iv) 5-(acridin-9-yl)-6-amino-1,3-dimethyl-uracil hydrochloride dihydrate (Kimura, 1987); their dimensions generally agree with those reported here.

Experimental

Crystal data

$C_6H_9N_3O_2$
$M_r = 155.15$
Orthorhombic
$Pmcn$
$a = 6.7004 (5)$ Å
$b = 7.1548 (5)$ Å
$c = 14.7572 (14)$ Å
$V = 707.5 (1)$ Å^3
$Z = 4$
$D_x = 1.46$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.7093$ Å
Cell parameters from 25 reflections
$\theta = 9.5 - 28.0°$
$\mu = 0.105$ mm^{-1}
$T = 293$ K
Block
$0.40 \times 0.30 \times 0.30$ mm
Colourless

Data collection

Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction:
  empirical
  $T_{min} = 0.77$, $T_{max} = 0.94$
842 measured reflections
842 independent reflections
636 observed reflections
  $[I_{net} > 3.0\sigma(I_{net})]$

$\theta_{max} = 27.0°$
$h = 0 \rightarrow 8$
$k = 0 \rightarrow 9$
$l = 0 \rightarrow 18$
3 standard reflections
  frequency: 60 min
  intensity variations: decay
  of 2.5% during data
  collection

Refinement

Refinement on F
$R = 0.043$
$wR = 0.071$
$S = 1.95$
636 reflections
68 parameters
H-atom parameters not
  refined
$w = 1/[\sigma^2(F) + 0.001F^2]$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.29$ e Å^{-3}
$\Delta\rho_{min} = -0.22$ e Å^{-3}
Atomic scattering factors
  from International Tables
  for X-ray Crystallogra-
  phy (1974, Vol. IV, Table
  2.2B)

Data collection: CAD-4 Software (Enraf–Nonius, 1989). Cell refinement: CAD-4 Software. Data reduction: NRCVAX DA-

TRD2 (Gabe, Le Page, Charland, Lee & White, 1988). Program(s) used to solve structure: NRCVAX SOLVER. Program(s) used to refine structure: NRCVAX LSTSQ. Molecular graphics: NRCVAX and ORTEPII (Johnson, 1976). Software used to prepare material for publication: NRCVAX TABLES.

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)

$$U_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
N(1)	0.25000	0.03879 (24)	0.23018 (13)	0.0321 (10)
N(3)	0.25000	−0.0589 (3)	0.07871 (13)	0.0360 (11)
N(6)	0.25000	0.3552 (3)	0.26783 (14)	0.0416 (12)
O(2)	0.25000	−0.2695 (3)	0.19290 (14)	0.0511 (12)
O(4)	0.25000	0.1532 (3)	−0.03610 (13)	0.0592 (14)
C(1)	0.25000	−0.0107 (4)	0.32617 (19)	0.0492 (16)
C(2)	0.25000	−0.1060 (4)	0.16851 (17)	0.0339 (12)
C(3)	0.25000	−0.2121 (4)	0.01354 (19)	0.0519 (17)
C(4)	0.25000	0.1262 (4)	0.04668 (16)	0.0381 (14)
C(5)	0.25000	0.2656 (4)	0.11318 (17)	0.0377 (13)
C(6)	0.25000	0.2230 (3)	0.20369 (15)	0.0305 (12)

Table 2. Geometric parameters (Å, °)

N(1)—C(1)	1.460 (3)	N(6)—C(6)	1.338 (3)
N(1)—C(2)	1.379 (3)	O(2)—C(2)	1.224 (3)
N(1)—C(6)	1.375 (3)	O(4)—C(4)	1.237 (3)
N(3)—C(2)	1.367 (3)	C(4)—C(5)	1.399 (4)
N(3)—C(3)	1.458 (3)	C(5)—C(6)	1.370 (3)
N(3)—C(4)	1.406 (3)		
O(2)...N(6^i)	2.903 (3)	N(6)···O(2^{iii})	2.904 (3)
O(4)···N(6^{ii})	2.894 (3)	N(6)···O(4^{iv})	2.894 (3)
C(1)—N(1)—C(2)	117.3 (2)	N(3)—C(2)—O(2)	121.4 (2)
C(1)—N(1)—C(6)	120.6 (2)	N(3)—C(4)—O(4)	118.6 (2)
C(2)—N(1)—C(6)	122.2 (2)	N(3)—C(4)—C(5)	115.8 (2)
C(2)—N(3)—C(3)	117.0 (2)	O(4)—C(4)—C(5)	125.5 (2)
C(2)—N(3)—C(4)	123.9 (2)	C(4)—C(5)—C(6)	121.7 (2)
C(3)—N(3)—C(4)	119.1 (2)	N(1)—C(6)—N(6)	118.5 (2)
N(1)—C(2)—N(3)	117.0 (2)	N(1)—C(6)—C(5)	119.4 (2)
N(1)—C(2)—O(2)	121.6 (2)	N(6)—C(6)—C(5)	122.2 (2)

Symmetry codes: (i) $x, y + 1, z$; (ii) $x, \tfrac{1}{2} - y, \tfrac{1}{2} + z$; (iii) $x, y - 1, z$; (iv) $x, \tfrac{1}{2} - y, -\tfrac{1}{2} - z$.

The ω-scan width was $(0.9 + 0.35\tan\theta)°$ with a θ-scan rate of $5.49°$ min^{-1} and background counts of 10 s on each side of every scan. The space group for (I) was determined from the systematic absences ($h0l$ absent if $l = 2n + 1$ and $hk0$ absent if $h + k = 2n + 1$) as either $P2_1cn$ (a non-standard setting of $Pna2_1$, No.29) or $Pmcn$ (a non-standard setting of $Pnma$, No.62). $Pmcn$ was indicated by analysis of the E statistics and this was confirmed by refinement. The amino H atoms were clearly visible in difference maps at an intermediate stage of the refinement and were positioned geometrically (N—H 0.95 Å) and included as riding atoms in the structure factor calculations. The H atoms attached to C atoms were treated similarly (C—H 0.95 Å), although those of the methyl groups were disordered.

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Structure of N1-(3-Phenoxypropyl)-4,7-diaza-1-azoniatricyclo[5.2.1.04,10]decane Bromide Hydrate

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Abstract

The structure of the title compound shows a distortion towards the amidinium form with the bond between the capping C atom and the quaternary N atom [1.668 (9) Å] being significantly longer than the distances between this C atom and the other two N atoms [1.419 (9) and 1.398 (9) Å].

Comment

The structure of the title compound was determined as it is an intermediate in the general preparative route to mono-*N*-substituted cyclic triazanonanes. It was prepared in near quantitative yield by allowing equimolar amounts of 1-bromo-3-phenoxypropane and 1,4,7-triazatricyclo[5.2.1.04,10]decane to react in tetrahydrofuran at room temperature in the dark (Atkins, 1980). The preparation of a related *N*-CH$_2$Ph derivative has been reported (Weisman, Vachon, Johnson & Gronbeck, 1987). The most

interesting feature of the structure concerns the bonding of the 'capping' C atom, C(1). Formally, the N(1) atom is a quaternary nitrogen as in (I), bearing

(I)   Br$^-$
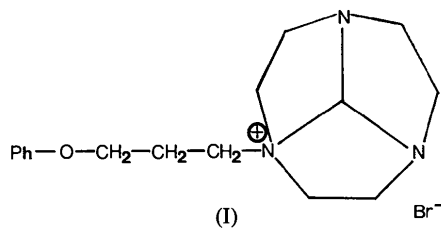
a positive charge, and has C—N—C angles in the range 102.3 (6)–116.1 (6)°. However, the structure shows considerable distortion towards the amidinium form, (II); the C(1)—N(1) distance

(II)   Br$^-$
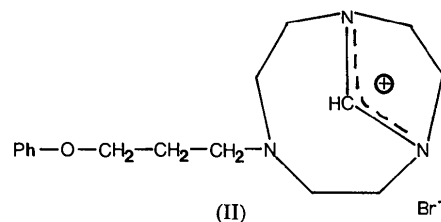
[1.668 (9) Å] is long for a C—N single bond and is significantly longer than C(1)—N(4) [1.419 (9) Å] and C(1)—N(7) [1.398 (9) Å]. These in turn are significantly shorter than the other C—N bond distances. The structure also contains water of solvation [O(2)] at less than full occupancy; least-squares refinement afforded a site occupancy factor of 0.72 (2).
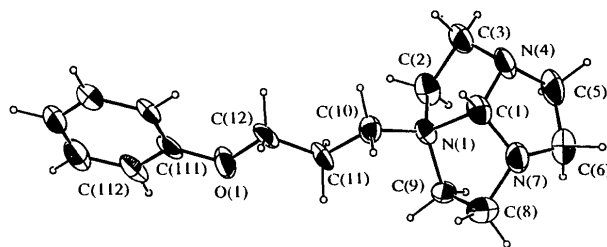

Fig. 1. Molecular structure and atomic labelling scheme for the cation. Thermal ellipsoids are shown at the 50% probability level and H atoms are shown as spheres of arbitrary radii.

Experimental

Crystal data

C$_{16}$H$_{24}$N$_3$O$^+$. Br$^-$.0.72H$_2$O	D_x = 1.38 Mg m^{-3}
M_r = 367.25	Mo Kα radiation
Monoclinic	λ = 0.71069 Å
P2$_1$/a	Cell parameters from 25
a = 8.431 (1) Å	reflections
b = 20.452 (3) Å	θ = 17–20°
c = 10.615 (3) Å	μ = 2.389 mm^{-1}
β = 111.42 (1)°	T = 298 K
	Cleaved from large prism