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Classical Packing and Stacking in 6-Phenyl-5-azauracil

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Abstract

Although probably not incorporated directly into nucleic acids, the title compound, 6-phenyl-1,3,5-triazine-

2,4(1*H*,3*H*)-dione ($C_9H_7N_3O_2$), resembles the pyrimidine bases in such nucleic acids. In the solid state, molecules base pair about a centre of symmetry into a dimer arrangement along the *a* axis and are linked firmly in the *c* direction by an N1—H1···O4 interaction related by the glide plane. The remaining intermolecular forces are achieved by the alternate stacking of phenyl and triazine rings in columns along the *b* axis.

Comment

Although the title compound, (1) (trivial name 6-phenyl-5-azauracil), has shown little biological activity, some azauracils have shown considerable promise in cancer chemotherapy. The parent compound, 5-azauracil, (2), is an antimetabolite (Suhadolnik, 1970) which inhibits the biosynthesis of pyrimidine bases and thus the production of nucleic acids (Adams & Davidson, 1981), whilst 6-azauracil has also revealed antineoplastic activity in animal tumours (Swindler & Welch, 1957). Since the extensive possibilities for hydrogen bonding in the triazinedione ring system in such compounds are likely to be important in such biological activity, the structure of (1) has been determined.
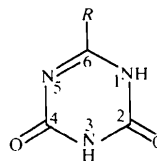
(1) *R* = Ph
(2) *R* = H

The two carbonyl bonds, C2=O2 and C4=O4, are almost equal in length [1.215 (1) and 1.218 (1) Å, respectively], thus confirming the diketo tautomeric form of the molecule in the solid state. Location of the H atoms at N1 and N3 by difference Fourier synthesis, together with the N5=C6 bond distance of 1.297 (2) Å confirms the correct assignment of protonation at these sites rather than at N5. In agreement with Chatar Singh's rule (Singh, 1965), an empirical form of the valence-shell electron-pair repulsion (VSEPR) theory (Gillespie, 1963), the ring bond angles at protonated N1 and N3 of 121.8 (1) and 124.6 (1)°, respectively, are much greater than the angle of 118.7 (1)° at the unprotonated N5 atom.

The angle of 7.2 (1)° between the least-squares planes of the triazine and phenyl rings could allow extensive conjugation, yet the degree to which electrons are attracted by the triazine ring from the phenyl ring seems very limited. The C6—C1′ bond length of 1.482 (2) Å is slightly longer than the average of 1.476 (14) Å for C_{sp^2}—C_{ar} bonds in conjugated C_{ar}—C=N—C systems (Allen *et al*., 1987). The packing arrangement of the molecules is shown in Fig. 2. Stacking produces infinite columns of molecules in the *b* direction with alternating

phenyl and triazine rings. The interplanar stacking distance of 3.31 (1) Å is similar to those found in 6-methylisocytosine [3.26 (1) Å; Lowe *et al.*, 1987], cytosine (3.36 Å; Barker & Marsh, 1964) and dihydrouracil (3.34 Å; Rohrer & Sundaralingam, 1970), and is characteristic of a normal van der Waals electrostatic interaction.
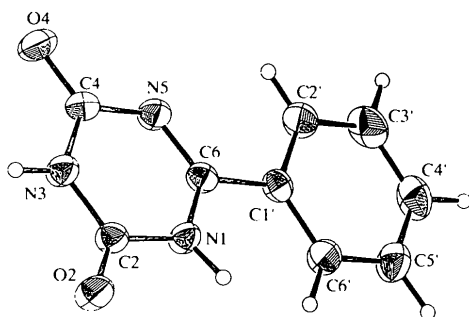

Fig. 1. *ORTEP*II (Johnson 1976) drawing of the title compound. Displacement ellipsoids are shown at the 50% probability level.
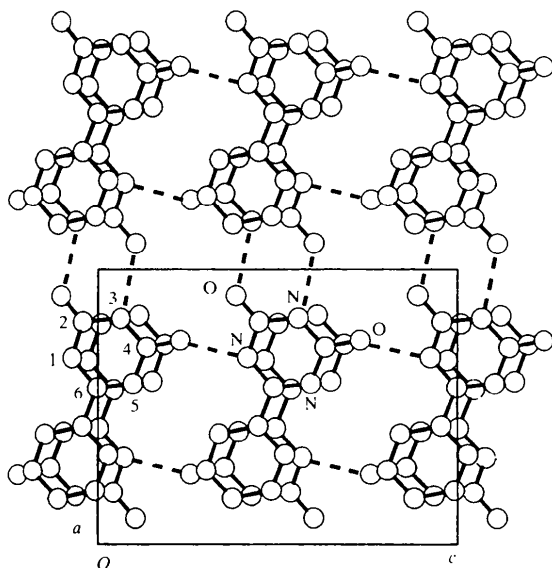

Fig. 2. *PLUTO* plot (Motherwell & Clegg, 1978) showing the packing of molecules as viewed down the *b* axis. All H atoms have been omitted for clarity and hydrogen bonds are shown as dashed lines.

The suggested hydrogen bonds are shown as dashed lines in Fig. 2 and the geometry and symmetry operations that characterize these are given in Table 2. Both carbonyl O atoms participate in strong hydrogen bonds. The N1—H1···O4 interaction [2.803 (1) Å] links chains of molecules related by the glide plane in the direction of the *c* axis, whilst the N3—H3···O2 interaction [2.845 (1) Å] produces a dimer base-pair arrangement along the *a* axis across a centre of symmetry. The net result is that the triazine ring is firmly anchored in four positions in the *a* and *c* directions by hydrogen bonding,

and in the *b* direction by classical stacking resulting in London force attraction. Such electrostatic interactions are reflected in the rather high melting point of this compound, *i.e.* 566–567 K.

Experimental

6-Phenyl-5-azauracil, (1), was prepared by treatment of the corresponding acyl biguanide with aqueous base. Crystallization from water produced colourless laths elongated along the *b* axis (m.p. 566–567 K).

Crystal data

$C_9H_7N_3O_2$	Mo $K\alpha$ radiation
$M_r = 189.18$	$\lambda = 0.71073$ Å
Monoclinic	Cell parameters from 25
$P2_1/c$	reflections
$a = 9.299\,(1)$ Å	$\theta = 8.68–22.41°$
$b = 7.279\,(3)$ Å	$\mu = 0.110$ mm^{-1}
$c = 12.404\,(1)$ Å	$T = 293\,(2)$ K
$\beta = 90.05\,(1)°$	Lath
$V = 839.6\,(4)$ Å^3	$0.60 \times 0.30 \times 0.15$ mm
$Z = 4$	Transparent, colourless
$D_x = 1.497$ Mg m^{-3}	
$D_m = 1.50$ Mg m^{-3}	
D_m measured by flotation in butan-1-ol and CCl$_4$	

Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{int} = 0.028$
$\omega/2\theta$ scans	$\theta_{max} = 26.99°$
Absorption correction: none	$h = 0 \rightarrow 11$
1921 measured reflections	$k = 0 \rightarrow 9$
1812 independent reflections	$l = -15 \rightarrow 15$
1396 reflections with	3 standard reflections
$I > 2\sigma(I)$	frequency: 120 min
	intensity decay: 1.4%

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.034$	$\Delta\rho_{max} = 0.220$ e Å^{-3}
$wR(F^2) = 0.096$	$\Delta\rho_{min} = -0.171$ e Å^{-3}
$S = 1.042$	Extinction correction:
1812 reflections	*SHELXL*93
156 parameters	Extinction coefficient:
All H atoms refined	0.054 (4)
$w = 1/[\sigma^2(F_o^2) + (0.0436P)^2 + 0.1588P]$	Scattering factors from *International Tables for Crystallography* (Vol. C)
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1. *Selected geometric parameters (Å, °)*

N1—C6	1.3665 (14)	C4—O4	1.2176 (15)
N1—C2	1.377 (2)	C4—N5	1.382 (2)
C2—O2	1.2153 (14)	N5—C6	1.2966 (15)
C2—N3	1.3619 (15)	C6—C1'	1.482 (2)
N3—C4	1.383 (2)		
N1—C6—C1'—C2'	−173.00 (12)		

C₉H₇N₃O₂

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···A	H···A	D···A	D—H···A
N1—H1···O4'	1.94 (2)	2.803 (1)	153 (1)
N3—H3···O2"	1.99 (2)	2.845 (1)	170 (2)

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

Although, from the cell parameters, the crystal symmetry appears to be very close to orthorhombic, Weissenberg and precession film data, together with diffractometer data, showed it to be monoclinic with a β angle very close to 90°.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *DATRED* (Brookhaven National Laboratory & Birmingham University, 1986). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *OR-TEP*II (Johnson, 1976) and *PLUTO* (Motherwell & Clegg, 1978). Software used to prepare material for publication: *SHELXL*93.

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Highly Strained C—C Bonds: 3-(1'-Hydroxy-4'-isopropyl-2',2'-dimethyl-1',2'-dihydrobenzocyclobuten-1'-yl)-3-methyl-2-butanone Ethylene Acetal, (I), and (3S*,1'S*)-3-Acetoxy-2-(1'-hydroxy-1',2'-dihydrobenzocyclobuten-1'-yl)-2-methylpentane, (II)†

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Abstract

The crystal structures of the title compounds, C₂₀H₃₀O₃ (I) and C₁₆H₂₂O₃ (II), are described. The benzocyclobutene rings in (I) and (II) are approximately planar. The lengths of the Csp^3—Csp^3 bonds in the cyclobutene rings of (I) and (II) are 1.659 (2) and 1.596 (2) Å, respectively. The C—C bond elongation observed in (I) may be ascribed to steric congestion and/or electronic effects on the bond exerted by the methyl groups and the alkyl side chain attached to the cyclobutenol moiety, together with a ring strain expected for a four-membered ring system.

Comment

Crystallographic and electronic structures of benzene derivatives fused to a strained small ring have been extensively studied (Boese & Bläser, 1988; Bläser *et al.*, 1989, 1994). In the crystal of benzocyclobutene, an elongated Csp^3—Csp^3 bond of 1.576 (1.580) Å was observed in the cyclobutene moiety which is coplanar to the benzene ring (Boese & Bläser, 1988). Recently, much longer Csp^3—Csp^3 bonds [1.710 (5)–1.724 (5) Å] were observed in the cyclobutene rings fused to naphthalene and anthracene rings (Toda *et al.*, 1996). In crystals of several benzocyclobutenol derivatives, C—C single bonds longer than 1.60 Å were also found in their cyclobutenol moieties (Courtois *et al.*, 1975, 1977, 1987; Ianelli *et al.*, 1990; Ianelli *et al.*, 1992a,b; Ianelli, Nardelli, Belletti, Jamart-Grégoire,

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