Acta Cryst. (1999). C**55**, 749–751

6-Acetylamino-5-(diacetylamino)-pyrimidine-2,4(1*H*,3*H*)-dione

John Nicolson Low,[a] George Ferguson,[b] Manuel Nogueras,[c] Adolfo Sánchez[c] and Justo Cobo[c]

[a]*AMRC, Department of Applied Physics and Electronic & Mechanical Engineering, University of Dundee, Dundee DD1 4HN, Scotland,* [b]*Department of Chemistry and Biochemistry, University of Guelph, Ontario, Canada N1G 2W1, and* [c]*Departamento Química Inorgánica y Orgánica, Facultad de Ciencias Experimentales, Universidad de Jaén, 23071 Jaén, Spain*

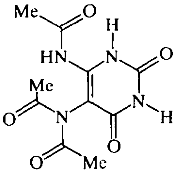
(*Received 19 November 1998; accepted 22 December 1998*)

Abstract

Molecules of the title compound, $C_{10}H_{12}N_4O_5$, are linked to generate sheets which lie in the *ab* plane at $z = 0,\frac{1}{2},1$ *etc.* by means of N—H···O intermolecular hydrogen bonds [N···O 2.844 (2)–3.232 (2) Å] and inversion centres. The 5-diacetamido group is oriented almost normal to the uracil plane [interplanar angle 87.1 (1)°] and the 6-acetamido group is held almost planar with the uracil plane [interplanar angle 7.1 (1)°] *via* an intramolecular N—H···O hydrogen bond [N···O 2.624 (2) Å].

Comment

The analysis of the structure of the title compound, (I), (also known as 6-acetamido-5-diacetamidouracil) is part of our continuing study of the molecular structures of 5,6-diaminopyrimidines and related derivatives. These compounds are of interest because of their potential biological activity and their value as intermediates in the preparation of other heterocyclic compounds. In this case the 5-acetamido group is used in the preparation of purine derivatives in cyclization reactions (Montgomery & Hewson, 1961; Fenn & Lister, 1974; Fernandez *et al.*, 1981; Melgarejo *et al.*, 1983). A view of (I) with our numbering scheme is shown in Fig. 1; principal molecular dimensions are in Table 1 and details of hydrogen bonding are in Table 2.



(I)

Normally, in uracil structures with 5- and 6-amino substituents, nitrogen N6 has very strong planar sp^2 character with the exocyclic C—N bond showing strong double-bond character, whilst N5 often has mainly pyramidal sp^3 character. That this depends critically on the nature of the groups attached to N5 is exemplified by the structure of (I), in this case N5 clearly has an essentially planar geometry [the sum of the angles around N5 is 359.30 (14)°]. The 5-diacetamido group is oriented almost normal to the uracil plane [interplanar angle 87.1 (1)°]. It has been pointed out previously (Beagley *et al.*, 1987) that the usual conformation of the carbonyls of the diacetamido group is *syn–anti*; in this present case it is *anti–anti* as a result of the acetyl O atoms both being involved (see below) in intermolecular hydrogen bonding. The 6-acetamido group is held almost planar with the uracil plane [interplanar angle 7.1 (1)°] *via* an intramolecular N1—H1···O61 hydrogen bond [N···O 2.624 (2) Å]. The related compound 6-acetylamino-4-methoxy-2-methylthiopyrimidine is completely planar with the molecule lying on a crystallographic mirror plane (Low *et al.*, 1996).

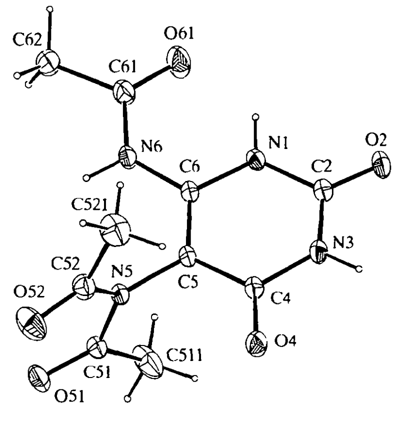


Fig. 1. A view of (I) with our numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Only the major orientations of the methyl-H atoms are shown.

The molecules pack (Fig. 2) to form base-paired dimers linked *via* N—H···O hydrogen bonds about inversion centres (at 0,0,0) *via* the usual base-pair interactions with N3—H3···O4[ii] [symmetry code: (ii) $-x$, $-y$, $-z$; Table 2); this is a common feature in nucleobase and nucleoside structures, *e.g.* in 5-bromo-2′-deoxycytidine (triclinic form) (Low *et al.*, 1981), 5-fluorocytosine (Louis *et al.*, 1982), 3′,5′-di-*O*-acetyl-5-bromo-2′-deoxyuridine (Low, 1983) and 3-

deazauracil (Low & Wilson, 1983). These dimers are then linked to form essentially planar zigzag ribbons which extend along the *b* direction by means of a bifurcated N—H···O hydrogen-bond system involving N1—H1···O61 and N1—H1···O61^{i} [symmetry code: (i) $-x$, $1-y$, $-z$] by use of, *e.g.*, the inversion centre at $(0,\frac{1}{2},0)$. The ribbons are linked to form infinite two-dimensional sheets which extend in the *ab* plane (at $z = 0,\frac{1}{2},1$ *etc.*) by utilizing a bifurcated hydrogen-bond system involving N6—H6 and both O atoms of the 5-diacetamido group related by the inversion centre at $(\frac{1}{4},\frac{1}{4},0)$ {N6—H6···O51^{iii} and N6—H6···O52^{iii} [symmetry code: (iii) $\frac{1}{2}-x$, $\frac{1}{2}-y$, $-z$]}. Examination of the structure with *PLATON* (Spek, 1998) showed that there were no solvent-accessible voids in the crystal lattice.

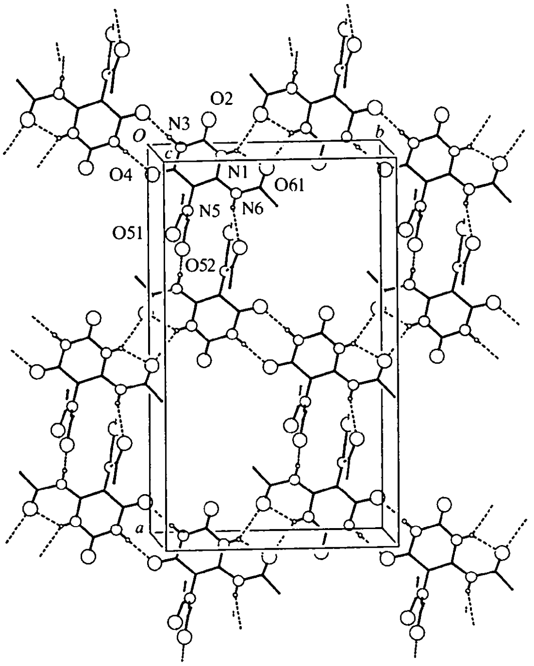


Fig. 2. A view showing part of the hydrogen-bonded sheet of molecules in the *ab* plane at $z = 0$ in the crystal structure of (I).

Experimental

Khmelevskii & Dumitsyna (1956) obtained the title compound in the acetylation of uric acid with acetic anhydride and pyridine. We have also prepared this compound in 43% yield starting from 5,6-diaminopyrimidine-2,4(1*H*,3*H*)-dione acetylated in Ac_2O and perchloric acid.

Crystal data

$C_{10}H_{12}N_4O_5$
$M_r = 268.24$
Monoclinic
*C*2/*c*
$a = 22.2132\ (15)$ Å
$b = 12.9986\ (13)$ Å
$c = 8.5456\ (5)$ Å
$\beta = 96.107\ (5)^\circ$
$V = 2453.5\ (3)$ Å^3
$Z = 8$
$D_x = 1.452$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 9.43–19.28^\circ$
$\mu = 0.118$ mm^{-1}
$T = 294\ (1)$ K
Needle
0.40 × 0.24 × 0.14 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
2873 measured reflections
2810 independent reflections
1814 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.021$
$\theta_{\rm max} = 27.43^\circ$
$h = -28 \rightarrow 28$
$k = 0 \rightarrow 16$
$l = 0 \rightarrow 11$
3 standard reflections
frequency: 120 min
intensity variation: 0.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.109$
$S = 1.025$
2810 reflections
179 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0511P)^2 + 0.7175P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.248$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.174$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997*a*)
Extinction coefficient: 0.0016 (4)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

C5—N5	1.4323 (19)	C6—N6	1.375 (2)
N5—C51	1.410 (2)	N6—C61	1.388 (2)
N5—C52	1.420 (2)		
N5—C5—C6	121.80 (14)	N1—C6—C5	120.04 (14)
C4—C5—N5	118.55 (14)	N1—C6—N6	117.36 (15)
C51—N5—C52	121.45 (14)	C5—C6—N6	122.59 (14)
C5—N5—C51	118.52 (14)	C6—N6—C61	126.98 (14)
C5—N5—C52	119.33 (14)		
O4—C4—C5—N5	−4.4 (3)	C2—N1—C6—N6	−176.7 (2)
N3—C4—C5—N5	175.9 (2)	N5—C5—C6—N1	−177.6 (2)
C6—C5—N5—C51	90.4 (2)	C4—C5—C6—N6	−175.7 (2)
C4—C5—N5—C51	−90.5 (2)	N5—C5—C6—N6	3.4 (3)
C6—C5—N5—C52	−99.0 (2)	N1—C6—N6—C61	2.1 (3)
C4—C5—N5—C52	80.1 (2)	C5—C6—N6—C61	−178.8 (2)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O61	0.86	1.97	2.624 (2)	132
N1—H1···O61^{i}	0.86	2.52	3.232 (2)	140
N3—H3···O4^{ii}	0.86	1.98	2.844 (2)	177
N6—H6···O51^{iii}	0.86	2.10	2.885 (2)	152
N6—H6···O52^{iii}	0.86	2.44	3.088 (2)	133

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

The space group of (I) was *C*2/*c* or *Cc* from the systematic absences, but *C*2/*c* was assumed and confirmed by the analysis. All H atoms were visible in difference maps. The H atoms of the three N—H groups appeared as well resolved peaks in the relevant C—N—C planes. The methyl-H atoms in each case showed maxima consistent with one major and one minor orientation; this was allowed for in the refinement during which all H atoms were treated as riding atoms (C—H 0.96 and N—H 0.86 Å). The methyl-H-atom occupancies refined to 0.85 (3)/0.15 (3), 0.84 (3)/0.16 (3) and 0.68 (3)/0.32 (3) for the C511, C512 and C62 methyl-H atoms, respectively.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1992). Cell refinement: *SET*4 and *CELDIM* (Enraf–Nonius, 1992). Data reduction: *DATRD*2 in *NRCVAX*96 (Gabe *et al.*, 1989). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*b*). Program(s) used to refine structure: *NRCVAX*96 and *SHELXL*97 (Sheldrick, 1997*a*). Molecular graphics: *NRCVAX*96, *ORTEP*II (Johnson, 1976) and *PLATON* (Spek, 1998). Software used to prepare material for publication: *NRCVAX*96, *SHELXL*97 and *PREP*8 (Ferguson, 1998).

We thank Dr J. F. Gallagher and Dublin City University for the funds to purchase the X-ray tube used in the data collections. While no direct support for the research described here was provided by NSERC (Canada), we do thank that organisation for the partial funding of the 1992 upgrade of the CAD-4 diffractometer.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1260). Services for accessing these data are described at the back of the journal.

References

Beagley, B., Flowers, W. T., Hafees, A. & Pritchard, R. G. (1987). *Acta Cryst.* C**43**, 1971–1973.
Enraf–Nonius (1992). *CAD*-4-*PC Software*. Version 1.1. Enraf–Nonius, Delft, The Netherlands.
Fenn, M. D. & Lister, J. H. (1974). *J. Chem. Soc. Perkin Trans.* 1, pp. 1300–1303.
Ferguson, G. (1998). *PREP*8. *A WordPerfect*-5.1 *Macro to Merge and Polish CIF Format Files from NRCVAX and SHELXL*97 *Programs*. University of Guelph, Canada.
Fernandez, A., Melgarejo, M., Robles, R., Sánchez, A. & Rico, R. (1981). *Nucleosides Nucleotides*, **8**, 325–329.
Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Khmelevskii, J. A. & Dumitsyna, O. I. (1956). *Zh. Obshch. Khim.* **26**, 755–760.
Louis, T., Low, J. N. & Tollin, P. (1982). *Cryst. Struct. Commun.* **11**, 1059–1064.
Low, J. N. (1983). *Acta Cryst.* C**39**, 796–798.
Low, J. N., Ferguson, G., Cobo, J., Melguizo, M., Nogueras, M. & Sanchez, A. (1996). *Acta Cryst.* C**52**, 2035–2037.
Low, J. N., Tollin, P. & Young, D. W. (1981). *Cryst. Struct. Commun.* **10**, 1369–1371.
Low, J. N. & Wilson, C. C. (1983). *Acta Cryst.* C**39**, 1688–1690.
Melgarejo, M., Robles, R., Rico, R. & Sánchez, A. (1983). *An. Quim. Ser. C*, **79**, 77–80.
Montgomery, J. A. & Hewson, K. (1961). *J. Org. Chem.* **26**, 4469–4472.
Sheldrick, G. M. (1997*a*). *SHELXL*97. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Sheldrick, G. M. (1997*b*). *SHELXS*97. *Program for the Solution of Crystal Structures*. University of Göttingen, Germany.
Spek, A. L. (1998). *PLATON*. *Molecular Geometry and Graphics Program*. Version of September 1998. University of Utrecht, The Netherlands.

Acta Cryst. (1999). C**55**, 751–754

2,2′-Biphenol–1,10-phenanthroline (1/1): a two-dimensional structure built up from three types of hydrogen bond and π–π stacking interactions

Emma S. Lavender, Richard M. Gregson, George Ferguson† and Christopher Glidewell

School of Chemistry, University of St Andrews, St Andrews, Fife KY16 9ST, Scotland. E-mail: cg@st-andrews.ac.uk

(*Received 5 January 1999; accepted 8 January 1999*)

Abstract

In the title compound, $C_{12}H_{10}O_2{\cdot}C_{12}H_8N_2$, there is an intramolecular O—H···O hydrogen bond within the 2,2′-biphenol component which is linked to the 1,10-phenanthroline component *via* a three-centre hydrogen bond involving both N atoms as acceptors. The bimolecular aggregates are linked by C—H···O hydrogen bonds into spiral chains along [010], and these, in turn, are linked into a sheet parallel to (101) by π–π stacking interactions between pairs of 1,10-phenanthroline units related by centres of inversion.

Comment

The heterocyclic diamine 2,2′-bipyridyl has been widely used as a chelating ligand for metal ions (Reedijk, 1987); in such an application, the two N atoms are necessarily located on the same edge of the near planar ligand. However, in pure 2,2′-bipyridyl, the molecules lie across centres of inversion, so that the N atoms lie on opposite edges (Merritt & Schroeder, 1956; Chisholm *et al.*, 1981). The ease of rotation about the central C—C bond is illustrated by the values of the dihedral angle between the two heteroaryl rings in hydrogen-bonded adducts of 2,2′-bipyridyl. In the 1:1 adduct with 4,4′-sulfonyldiphenol, the 2,2′-bipyridyl molecule has a conformation close to *trans*-planar, with a dihedral angle of 8.4 (1)° (Lavender *et al.*, 1998*a*), while in the 1:2 adduct with 1,3,5-trihydroxybenzene, the two independent 2,2′-bipyridyl molecules are again close to *trans*-planar in conformation, with dihedral angles of 15.0 (1) and 14.7 (1)° (Lavender *et al.*, 1998*b*). In contrast, when 2,2′-bipyridyl molecules are captured in the cavity formed by paired C-methylcalix[4]resorcinarene molecules, the dihedral angle is 40.4 (1)° (Ferguson *et al.*, 1998).

---

† On sabbatical leave from Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1.