References

Brenchley, G., Fedouloff, M., Mahon, M. F., Molloy, K. C. & Wills, M. (1995). *Tetrahedron*, **51**, 10581–10592.

Bryan, P. S. & Kuczkowski, R. L. (1972). *Inorg. Chem.* **11**, 553–559.

Duchamp, D. J. (1964). *Am. Crystallogr. Assoc. Meet., Bozeman, Montana*, Paper B14, pp. 29–30.

Enders, D., Berg, T., Raabe, G. & Runsink, J. (1996). *Helv. Chim. Acta*, **79**, 118–122.

Enraf–Nonius (1989). *CAD-4 Software*. Version 5. Enraf–Nonius, Delft, The Netherlands.

Gourdel, Y., Ghanimi, A., Pellon, P. & Le Corre, M. (1993). *Tetrahedron Lett.* **34**, 1011–1012.

Huffman, J. C., Skupinsky, W. A. & Caulton, K. G. (1982). *Cryst. Struct. Commun.* **11**, 1435–1440.

Imamoto, T. (1993). *Pure Appl. Chem.* **65**, 655–660.

Imamoto, T. & Hikosaka, T. (1994). *J. Org. Chem.* **59**, 6753–6759.

Imamoto, T., Kusumoto, T., Suzuki, N. & Sato, K. (1985). *J. Am. Chem. Soc.* **107**, 5301–5303.

Imamoto, T., Oshiki, T., Onozawa, T., Kusumoto, T. & Sato, K. (1990). *J. Am. Chem. Soc.* **112**, 5244–5252.

McKinstry, L. & Livinghouse, T. (1994). *Tetrahedron Lett.* **35**, 9319–9322.

McKinstry, L. & Livinghouse, T. (1995). *Tetrahedron*, **51**, 7655–7666.

Mohr, B., Lynn, D. M. & Grubbs, R. H. (1996). *Organometallics*. In preparation.

Schmidbaur, H. & Weiss, E. (1981). *Angew. Chem. Int. Ed. Engl.* **20**, 283–284.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Acta Cryst. (1996). C**52**, 3108–3110

6-Bromo-2*H*-3,1-benzoxazine-2,4(1*H*)-dione at 153 K

PAOLO LUBINI[a] AND JOHAN WOUTERS[b]

[a]*Institut für Anorganische Chemie der Universität Göttingen, Tammannstrasse 4, D-37077 Göttingen, Germany, and* [b]*Laboratoire de Chimie Moléculaire Structurale, Facultés N.-D. de la Paix, 61 Rue de Bruxelles, B-5000 Namur, Belgium. E-mail: wouters@scf.fundp.ac.be*

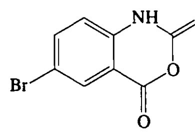
(*Received 4 April 1996; accepted 2 July 1996*)

Abstract

The crystal structure of the title compound, $C_8H_4BrNO_3$, was determined at 153 K. The structure was solved by direct methods and refined by least-squares calculations to a final R value of 0.056. The molecular geometry is similar to that of the parent non-brominated compound but the crystal packing differs.

Comment

The title compound, (I), crystallizes in space group $Pna2_1$ with one molecule in the asymmetric unit. The molecule is planar (the r.m.s. deviation from the best plane through all the atoms is 0.019 Å, with a maximum deviation of 0.045 Å for O2).


(I)

The distances as well as the angles are generally as expected. The molecular geometry adopted is very similar to that observed in the parent compound without the Br atom (Kashino, Nakashima & Haisa, 1978) but the crystal packing displays some different features. In the non-brominated structure, the packing results from the stacking of dimers held together by hydrogen bonds between N and O2. In the present structure, these dimers

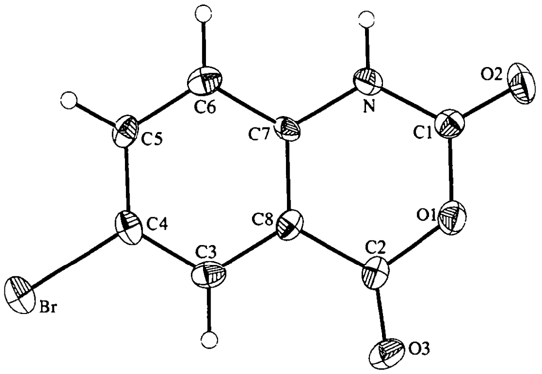


Fig. 1. Molecular structure of the title compound. Non-H atoms are represented by displacement ellipsoids at the 50% probability level. The atomic numbering scheme used in the paper is shown and is equivalent to the one used by Kashino *et al.* (1978) for the non-brominated compound.

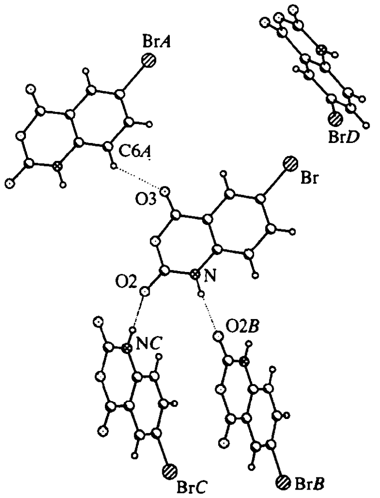


Fig. 2. View of the crystal packing of the title compound. For clarity, only the molecules surrounding the central one are displayed.

are not observed. N and O2 are still involved in hydrogen bonds but in this case, the interactions affect more than two molecules. Molecules lying in the same plane are held together by C—H···O interactions. In addition, the C4—Br bond is almost normal to the plane of a symmetry-related molecule with the Br atom at 3.3 Å from this plane. The distance between stacking molecules is also about 3.3 Å.

Experimental

Thin plate-shaped crystals of the title compound (Fluka) were grown from a saturated solution in THF.

Crystal data

$C_8H_4BrNO_3$
$M_r = 242.03$
Orthorhombic
$Pna2_1$
$a = 24.904$ (5) Å
$b = 6.0290$ (12) Å
$c = 5.1640$ (10) Å
$V = 775.4$ (3) Å^3
$Z = 4$
$D_x = 2.073$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 68 reflections
$\theta = 10–12.5°$
$\mu = 5.268$ mm^{-1}
$T = 153$ (2) K
Thin plate
0.65 × 0.45 × 0.04 mm
Orange

Data collection

Stoe *P*4 diffractometer
$\theta/2\theta$ scans
Absorption correction:
ψ scan (North, Phillips & Mathews, 1968)
$T_{\min} = 0.295$, $T_{\max} = 0.813$
1514 measured reflections
1348 independent reflections

1223 observed reflections [$I > 2\sigma(I)$]
$R_{\rm int} = 0.061$
$\theta_{\max} = 25°$
$h = -29 \rightarrow 29$
$k = -7 \rightarrow 7$
$l = -6 \rightarrow 6$
3 standard reflections
frequency: 90 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0559$
$wR(F^2) = 0.1424$
$S = 1.026$
1348 reflections
118 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.1126P)^2 + 0.7760P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.476$ e Å^{-3}
$\Delta\rho_{\min} = -0.422$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Absolute configuration: Flack (1983)
Flack parameter = −0.01 (3)

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

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

	x	y	z	$U_{\rm eq}$
Br	0.73941 (3)	0.55628 (11)	0.9741 (3)	0.0278 (3)
N	0.5494 (3)	0.1898 (9)	1.5616 (11)	0.0204 (14)
O1	0.5491 (2)	0.4954 (8)	1.8364 (11)	0.0233 (12)
C1	0.5274 (3)	0.2966 (11)	1.7646 (14)	0.0182 (15)
O2	0.4905 (2)	0.2278 (8)	1.8923 (11)	0.0283 (14)
C2	0.5909 (3)	0.5987 (12)	1.7063 (13)	0.0187 (16)
C3	0.6588 (3)	0.5592 (11)	1.3602 (15)	0.0197 (16)
O3	0.6045 (2)	0.7777 (8)	1.7822 (11)	0.0258 (13)
C4	0.6798 (3)	0.4385 (10)	1.1602 (15)	0.0185 (15)
C5	0.6593 (3)	0.2313 (12)	1.0897 (13)	0.0178 (15)
C6	0.6156 (3)	0.1465 (12)	1.2221 (14)	0.0198 (16)
C7	0.5934 (3)	0.2683 (10)	1.4252 (13)	0.0150 (15)
C8	0.6151 (3)	0.4728 (10)	1.4968 (17)	0.0167 (14)

Table 2. *Selected geometric parameters (Å, °)*

Br—C4	1.905 (8)	C2—C8	1.452 (10)
N—C1	1.346 (9)	C3—C4	1.368 (11)
N—C7	1.387 (9)	C3—C8	1.397 (11)
O1—C1	1.366 (9)	C4—C5	1.398 (10)
O1—C2	1.386 (10)	C5—C6	1.383 (11)
C1—O2	1.206 (9)	C6—C7	1.394 (10)
C2—O3	1.197 (9)	C7—C8	1.396 (9)
C1—N—C7	123.6 (6)	C3—C4—Br	118.8 (5)
C1—O1—C2	124.0 (6)	C5—C4—Br	119.1 (6)
O2—C1—N	124.9 (7)	C6—C5—C4	119.3 (7)
O2—C1—O1	117.1 (7)	C5—C6—C7	119.2 (6)
N—C1—O1	118.0 (7)	N—C7—C6	121.0 (6)
O3—C2—O1	117.3 (7)	N—C7—C8	118.2 (6)
O3—C2—C8	126.7 (7)	C6—C7—C8	120.8 (7)
O1—C2—C8	116.0 (6)	C7—C8—C3	119.7 (7)
C4—C3—C8	118.8 (6)	C7—C8—C2	119.9 (7)
C3—C4—C5	122.1 (7)	C3—C8—C2	120.3 (6)

D—H···A	D—H	H···A	D···A	D—H···A
N—H1···O2$^{\rm i}$	0.880	1.967	2.845	174.7
C6—H6···O3$^{\rm ii}$	0.950	2.457	3.191	134.0

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

The crystal selected for data collection was first washed with THF to clean its faces and mounted on a quartz fibre. Data were collected at 153 K. *DIF*4 (Stoe & Cie, 1990*a*) software was used for data collection and cell refinement. Corrections for background, decay, Lorentz and polarization effects were included in the data reduction using *REDU*4 (Stoe & Cie, 1990*b*). Absorption effects were important owing to the presence of a Br atom and to the shape of the crystal; a semi-empirical (ψ scan producing 338 reflections at χ greater than 75°) absorption correction was applied to the data (North, Phillips & Mathews, 1968). It is recognised that the absorption correction is not optimal, but it was the only one available at the time of the study. The structure was solved by direct methods with the program *SHELXS*86 (Sheldrick, 1990), which resulted in reliable positions for all 13 non-H atoms. The initial model was refined by least-squares techniques with *SHELXL*96 (Sheldrick, 1996). Non-H atoms were refined with anisotropic displacement parameters. The positions of the H atoms were refined using a riding model. *SHELXTL/PC* (Sheldrick, 1992) was used for molecular graphics. *SHELXL*96 was used to prepare the material for publication. Most machine calculations were conducted on an IBM RS6000.

JW thanks the National Foundation for Scientific Research (FNRS Belgium) for his Research Assistant position, and the Boehringer Ingelheim Fonds for partial financial support of his post-doctoral stay in Professor Sheldrick's group. PL thanks the European Community for a post-doctoral grant (BBW 94.0162 CHBG CT 940731)

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: DU1159). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Kashino, S., Nakashima, S. & Haisa, M. (1978). *Acta Cryst.* B**34**, 2191–2195
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1992). *SHELXTL/PC*. Version 4.3. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1996). *SHELXL96. Program for the Refinement of Crystal Structures*. *β* test version. University of Göttingen, Germany.
Stoe & Cie (1990*a*). *DIF*4. *Diffractometer Control Program*. Version 7.09/DOS. Stoe & Cie, Darmstadt, Germany.
Stoe & Cie (1990*b*). *REDU*4. *Data Reduction Program*. Version 7.03/DOS. Stoe & Cie, Darmstadt, Germany.

Acta Cryst. (1996). C**52**, 3110–3112

6-Amino-1,3-dimethyl-5-(4-oxo-2-penten-2-yl)aminouracil

Sonia B. Jimenez-Pulido,[a] John N. Low,[b] George Ferguson,[c] Miguel N. Moreno-Carretero[a] and Francisco Hueso-Ureña[a]

[a]*Departamento Química Inorgánica y Orgánica, Facultad de Ciencias Experimentales, Universidad de Jaén, 23071-Jaén, Spain,* [b]*Department of Applied Physics and Electronic & Mechanical Engineering, University of Dundee, Dundee DD1 4HN, Scotland, and* [c]*Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1. E-mail: j.n.low@dundee.ac.uk*

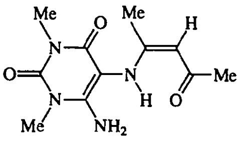
(*Received 26 July 1996; accepted 2 September 1996*)

Abstract

The title compound, $C_{11}H_{16}N_4O_3$ [6-amino-1,3-dimethyl-5-(4-oxo-2-penten-2-yl)amino-2,4(1*H*,3*H*)-pyrimidinedione], shows extensive delocalization in the uracil ring. There is an intramolecular hydrogen bond [N···O 2.713 (3) Å] between an amino N—H group and an adjacent carbonyl-O atom. The molecules are linked into sheets that are parallel to the $(10\bar{1})$ plane by intermolecular N—H···O hydrogen bonds [N···O 2.805 (3) and 2.803 (3) Å].

Comment

The bonds and angles of the title compound, (I) (Fig. 1), are very similar to those found for 6-amino-1,3-dimethyluracil (Ferguson *et al.*, 1993) and 6-amino-1,3-dimethyl-5-hydroxyiminomethyluracil (Low, Ferguson, Moreno-Carretero & Hueso-Ureña, 1994). Principal dimensions are in Table 2; the C6—N6 bond [1.336 (3) Å] shows the typical intermediate single–double-bond character as found in the compounds cited above as well as in other 6-aminouracil derivatives. The mean plane of the side chain (N5, C51, C53, C54, O5) attached to C5 is tilted at 75.3 (1)° to that of the pyrimidine base (N1, C2, N3, C4, C5, C6). The deviations for the former mean plane range from −0.024 (2) (for C54) to 0.026 (2) Å (for C53); those for the pyrimidine base are in the range −0.018 (2) (for C4) to 0.023 (2) Å (for N3). The N5—H···O5 intramolecular hydrogen bond (Fig. 1, Table 3) is responsible for the planarity of the atoms of the C5 side chain.



(I)

O—H···N hydrogen bonds link the molecules into infinite chains by operation of the *n*-glide and into infinite spirals along the **b** direction from a 2_1 screw operation (Table 3). The combination of both of these results in sheets of molecules which are parallel to the $(10\bar{1})$ plane (Fig. 2). There are only normal van der Waals interactions between the sheets. Examination of

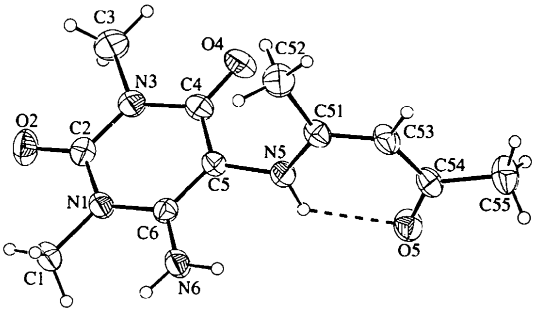


Fig. 1. A view of (I) with our numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

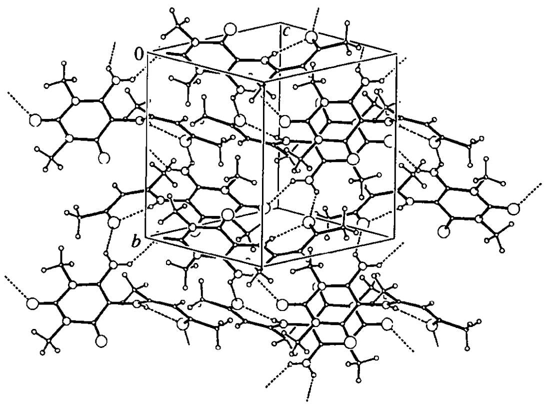


Fig. 2. Packing diagram of the molecule showing the hydrogen bonding.