

Acta Crystallographica Section C

**Crystal Structure
Communications**

ISSN 0108-2701

***N*-(6-Bromo-4-oxo-3,4-dihydropteridin-2-yl)-2,2-dimethylpropanamide**

S. Shanmuga Sundara Raj *et al.*

Electronic paper

This paper is published electronically. It meets the data-validation criteria for publication in Acta Crystallographica Section C. The submission has been checked by a Section C Co-editor though the text in the 'Comments' section is the responsibility of the authors.

© 2000 International Union of Crystallography • Printed in Great Britain – all rights reserved

N-(6-Bromo-4-oxo-3,4-dihydropteridin-2-yl)-2,2-dimethylpropanamide

S. Shanmuga Sundara Raj,^a Ibrahim Abdul Razak,^a
Hoong-Kun Fun,^{a*} Shyamaprosad Goswami,^b Reshmi
Mukherjee^b and Avijit Adak^b

^aX-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia, and ^bDepartment of Chemistry, Bengal Engineering College, Botanic Garden, Howrah 711 103, India
Correspondence e-mail: hkfun@usm.my

Received 8 May 2000

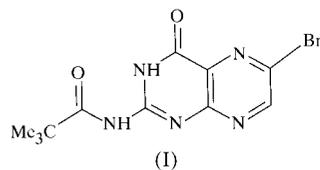
Accepted 30 May 2000

Data validation number: IUC0000153

In the title compound, C₁₁H₁₂BrN₅O₂, the rings in the pterin moiety are planar. The carbonyl O atom is in a synperiplanar conformation, while the C–N–C(=O)–C linkage is anti-periplanar. N–H···N and N–H···O intermolecular hydrogen bonds transform the molecules into infinite chains.

Comment

Pterin exists in polymeric structures, and folates having pterin moieties also exist as cyclic hydrogen-bonded tetramers which also form a liquid-crystal mesophase (Mariani *et al.*, 1989; Bonazzi *et al.*, 1991). Almost all naturally occurring pterins (*e.g.* biopterin, neopterin, folic acid *etc.*) possess a substituent at the 6-position of the pterin ring. The difficulty in getting a single crystal of the pterin molecule is due to its notorious insolubility in common organic solvents and also in water. The introduction of a *tert*-butyl group (*e.g.* pivaloyl pterin) enhances its solubility by breaking the stronger hydrogen-bonded polymeric network arrangement of the pterin molecule. We report here the hydrogen-bonding network in the crystal structure of 2-pivaloyl-6-bromopterin, (I), as an example of a 6-substituted soluble pterin derivative.



The bond lengths and angles observed in the pterin moiety are comparable to the reported values (Nasir *et al.*, 1992). The fused rings in the pterin moiety are planar, with the Br1 and O1 atoms deviating from the mean plane by –0.082 (1) and 0.132 (4) Å, respectively. The carbonyl O2 atom is in a

synperiplanar conformation with respect to C5, while the conformation observed across the C5–N5–C7–C8 linkage is antiperiplanar. The geometry and conformational features resemble those of the chlorpterin derivative (Goswami *et al.*, 2000). In the crystal, the N3 and N5 atoms are involved in N3–H3A···N4($x, \frac{3}{2} - y, -\frac{1}{2} + z$) and N5–H5A···O1($x, \frac{3}{2} - y, \frac{1}{2} + z$) intermolecular hydrogen bonds. These hydrogen bonds form eight-membered hydrogen-bonded rings at each side of the molecules, each of which has the graph-set motif of $R_2^2(8)$ (Bernstein *et al.*, 1995). These rings link the molecules into infinite chains in the [001] direction.

Experimental

2-Amino-6-bromopterin (100 mg, 41 mmol) and 4-(dimethylamino)pyridine (10 mg) in pivalic anhydride (3 ml) were stirred at 353 K for 12 h. The excess pivalic anhydride and pivalic acid were removed carefully through short-path distillation under reduced pressure. The brown product was washed well with sodium carbonate (5% solution) followed by water and extracted with chloroform. The organic layer was evaporated under reduced pressure. The product was prepared by silica gel (60–120 mesh) eluting with 1% methanol in chloroform which yielded pure 2-pivaloylamino-6-bromopterin (120 mg, 90%). The compound was recrystallized from a methylene chloride and methanol mixture (3:2 *v/v*).

Crystal data

C ₁₁ H ₁₂ BrN ₅ O ₂	$D_x = 1.578 \text{ Mg m}^{-3}$
$M_r = 326.17$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 4433 reflections
$a = 13.4315 (1) \text{ \AA}$	$\theta = 1.58\text{--}28.32^\circ$
$b = 10.3779 (2) \text{ \AA}$	$\mu = 3.00 \text{ mm}^{-1}$
$c = 10.2560 (2) \text{ \AA}$	$T = 293 (2) \text{ K}$
$\beta = 106.216 (1)^\circ$	Slab, yellow
$V = 1372.72 (4) \text{ \AA}^3$	$0.36 \times 0.26 \times 0.22 \text{ mm}$
$Z = 4$	

Data collection

Siemens SMART CCD area-detector diffractometer	3332 independent reflections
ω scans	1999 reflections with $I > 2\sigma(I)$
Absorption correction: empirical (SADABS; Sheldrick, 1996)	$R_{\text{int}} = 0.067$
$T_{\text{min}} = 0.381, T_{\text{max}} = 0.517$	$\theta_{\text{max}} = 28.22^\circ$
9400 measured reflections	$h = -17 \rightarrow 17$
	$k = -13 \rightarrow 13$
	$l = -13 \rightarrow 12$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.054$	$w = 1/[\sigma^2(F_o^2) + (0.0873P)^2]$
$wR(F^2) = 0.128$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.935$	$(\Delta/\sigma)_{\text{max}} < 0.001$
3332 reflections	$\Delta\rho_{\text{max}} = 0.76 \text{ e \AA}^{-3}$
200 parameters	$\Delta\rho_{\text{min}} = -0.91 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Br1–C2	1.886 (4)	N3–C5	1.361 (4)
O1–C4	1.228 (4)	N3–C4	1.379 (4)
O2–C7	1.204 (4)	N4–C5	1.301 (4)
N1–C1	1.325 (5)	N4–C6	1.380 (4)
N1–C6	1.358 (4)	N5–C5	1.378 (4)
N2–C2	1.391 (5)	N5–C7	1.390 (4)
N2–C3	1.401 (5)		
C5–N5–C7	127.1 (3)	O2–C7–C8	122.4 (3)
O2–C7–N5	121.2 (3)	N5–C7–C8	116.4 (3)

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

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N3—H3A \cdots O2	0.86	2.08	2.680 (4)	126
N3—H3A \cdots N4 ⁱ	0.86	2.30	3.003 (4)	140
N5—H5A \cdots O1 ⁱⁱ	0.86	2.13	2.958 (4)	163

Symmetry codes: (i) $x, \frac{3}{2}-y, z-\frac{1}{2}$; (ii) $x, \frac{3}{2}-y, \frac{1}{2}+z$.

All the H atoms were fixed at calculated positions and allowed to ride on the parent atoms. The *tert*-butyl group was found to have rotational disorder with occupancy of 52:48.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 1990).

The authors would like to thank the Malaysian Government and Universiti Sains Malaysia for research grant R&D No.

305/pfizik/610942. SSSR thanks the Universiti Sains Malaysia for a Visiting Postdoctoral Fellowship.

References

- Bernstein, J., Davis, R. E., Shimoni, L. & Chang N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
- Bonazzi, S., Capobianco, M., De Morais, M. M., Garbesi, A., Gottarelli, G., Mariani, P., Bossi, M. G. P., Spada, G. P. & Tondelli, L. (1991). *J. Am. Chem. Soc.* **113**, 5809.
- Goswami, S., Mukherjee, R., Ghosh, K., Razak, I. A., Shanmuga Sundara Raj, S. & Fun, H.-K. (2000). *Acta Cryst.* **C56**, 477–478.
- Mariani, P., Mazabard, C., Garbesi, A. & Spada, G. P. (1989). *J. Am. Chem. Soc.* **111**, 6369.
- Nasir, M. S., Karlin, K. D., Chen, Q. & Zubieta, J. (1992). *J. Am. Chem. Soc.* **114**, 2264–2265.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997). *SHELXTL Software Reference Manual*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.
- Siemens (1996). *SMART* and *SAINT* (Version 4) *Software Reference Manuals*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Spek, A. L. (1990). *Acta Cryst.* **A46**, C-34.