

Self-assembly of 2-pivaloyl-6-chloro-
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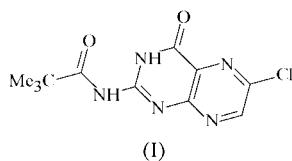
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In the title compound, *N*-(6-chloro-4-oxo-3,4-dihydropteridin-2-yl)-2,2-dimethylpropanamide, C₁₁H₁₂ClN₅O₂, the rings in the pterin moiety are planar. The amide carbonyl O atom is in syn-periplanar conformation while the C–N–C–C propanamide linkage is antiperiplanar. The N–H···N and N–H···O intermolecular hydrogen bonds transform the molecules into infinite chains.

Comment

Pterins exist 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.* bipterin, 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. 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-chloropterin, (I), as an example of a 6-substituted soluble pterin derivative. The special features of this unique system are shown in its crystal structure, a hydrogen-bonded self-assembly which includes Cl···Cl interactions holding the pterin layers together.



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 Cl1 and O1

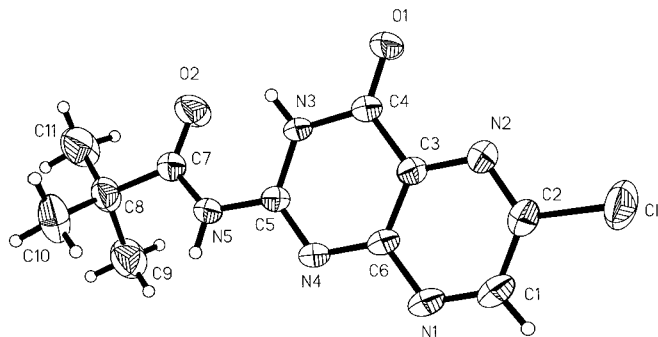


Figure 1
The structure of (I) showing 50% probability displacement ellipsoids and the atom-numbering scheme.

atoms deviating from the mean plane by 0.123 (1) and 0.192 (2) Å, respectively. The amide carbonyl O atom is in syn-periplanar conformation with respect to C5 while the conformation observed across the C–N–C–C propanamide linkage is antiperiplanar (Fig. 1).

In the crystal, the N3 and N5 atoms formed N3–H1N3···N4($x, \frac{3}{2} - y, z - \frac{1}{2}$) and N5–H1N5···O1($x, \frac{3}{2} - y, \frac{1}{2} + z$) intermolecular hydrogen bonds (Fig. 2). These N–H···N and N–H···O intermolecular 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). Both eight-membered rings are twisted with the angle between the two four-atom planes being 45.8 (2)°. The mean plane through the first eight-membered ring, which contains N3 and N4($x, \frac{3}{2} - y, z - \frac{1}{2}$), makes a dihedral angle of 4.5 (1) and 28.25 (8)° with the mean plane of the other eight-membered ring [*i.e.* with N5 and O1($x, \frac{3}{2} - y, \frac{1}{2} + z$)] and the planar-fused ring in the pterin moiety, respectively. These rings translated the molecules into infinite chains

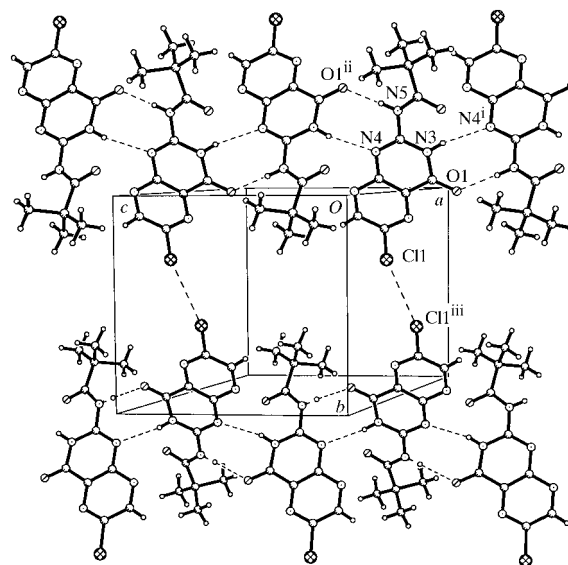


Figure 2
Layers of infinite chains connected through Cl···Cl interactions [symmetry codes: (i) $x, \frac{3}{2} - y, z - \frac{1}{2}$; (ii) $x, \frac{3}{2} - y, \frac{1}{2} + z$; (iii) $1 - x, -y, 1 - z$].

in the [001] direction. The Cl—Cl interactions hold these chains together along the *b* axis.

Experimental

2-Amino-6-chloropteridine was pivaloylated by heating with pivalic anhydride in dimethylformamide at 343 K for 7 h. The usual workup and purification of 2-pivaloylamino-6-chloropteridine by chromatography over silica gel [CHCl₃—CH₃OH (99:1)] afforded pure 2-pivaloylamino-6-chloropteridine which was directly used for crystallization using chloroform as the crystallizing solvent.

Crystal data

C ₁₁ H ₁₂ ClN ₅ O ₂	$D_x = 1.455 \text{ Mg m}^{-3}$
$M_r = 281.71$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 4762 reflections
$a = 13.5984 (5) \text{ \AA}$	$\theta = 1.58\text{--}28.32^\circ$
$b = 9.6927 (3) \text{ \AA}$	$\mu = 0.303 \text{ mm}^{-1}$
$c = 10.3211 (4) \text{ \AA}$	$T = 293 (2) \text{ K}$
$\beta = 108.981 (1)^\circ$	Slab, colourless
$V = 1286.41 (8) \text{ \AA}^3$	$0.40 \times 0.22 \times 0.12 \text{ mm}$
$Z = 4$	

Data collection

Siemens SMART CCD area-detector diffractometer	3166 independent reflections
ω scans	2235 reflections with $I > 2\sigma(I)$
Absorption correction: empirical (SADABS; Sheldrick, 1996)	$R_{\text{int}} = 0.053$
$T_{\text{min}} = 0.888$, $T_{\text{max}} = 0.965$	$\theta_{\text{max}} = 28.28^\circ$
8666 measured reflections	$h = -18 \rightarrow 17$
	$k = -12 \rightarrow 10$
	$l = -12 \rightarrow 13$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0678P)^2 + 0.4544P]$
$R[F^2 > 2\sigma(F^2)] = 0.055$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.157$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.07$	$\Delta\rho_{\text{max}} = 0.28 \text{ e \AA}^{-3}$
3166 reflections	$\Delta\rho_{\text{min}} = -0.48 \text{ e \AA}^{-3}$
212 parameters	
H atoms: see text	

Table 1

Selected geometric parameters (\AA , $^\circ$).

O1—C4	1.217 (3)	N3—C4	1.381 (3)
N1—C1	1.312 (3)	N4—C5	1.303 (3)
N1—C6	1.358 (3)	N4—C6	1.369 (3)
N2—C2	1.306 (3)	C1—C2	1.399 (4)
N2—C3	1.352 (3)	C3—C6	1.400 (3)
N3—C5	1.363 (3)	C3—C4	1.466 (3)
C5—N5—C7—O2	−5.2 (4)	C5—N5—C7—C8	173.5 (2)

Table 2

Hydrogen-bonding geometry (\AA , $^\circ$).

$D\text{---}H\cdots A$	$D\text{---}H$	$H\cdots A$	$D\cdots A$	$D\text{---}H\cdots A$
N3—H1N3 \cdots N4 ⁱ	0.82 (3)	2.30 (3)	3.053 (3)	154 (3)
N5—H1N5 \cdots O1 ⁱⁱ	0.84 (3)	2.14 (3)	2.954 (3)	164 (3)

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

All H atoms were located from a difference Fourier map and refined isotropically, except for H atoms of the *tert*-butyl group, which were geometrically fixed and allowed to ride on their attached atoms. The C—H distance in the pteridine ring refined to 0.86 (3) \AA . The *tert*-butyl group was found to have orientational disorder with occupancy of 60:40.

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; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL, PARST (Nardelli, 1995) and PLATON (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1368). Services for accessing these data are described at the back of the journal.

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