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1,3,7-Trimethyl-2,4-dioxo-1,2,3,4-tetrahydropteridine-6-carboxylic acid hemihydrate

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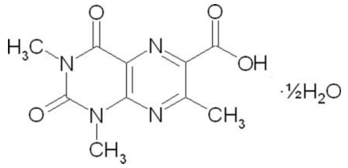
Key indicators: single-crystal X-ray study; T = 120 K; mean σ(C–C) = 0.003 Å; R factor = 0.055; wR factor = 0.140; data-to-parameter ratio = 10.9.

In the title compound, $C_{10}H_{10}N_4O_4{\cdot}0.5H_2O$, the two rings of the pteridine system are nearly coplanar [dihedral angle = 4.25 (9)°]. The atoms of the carboxyl group are also coplanar with the pteridine unit [r.m.s. deviation from the mean plane of the pteridine skeleton = 0.092 (2) Å]. In the crystal, the presence of the water molecule of crystallization (O atom site symmetry 2) leads to a hydrogen-bonding pattern different from the one shown by many carboxylic acid compounds (dimers formed through O—H$\cdots$O hydrogen bonds between neighbouring carboxyl groups): in the present structure, the water molecule, which lies on a binary axis, acts as a bridge between two molecules, forming a hydrogen-bonded dimer. In addition to the hydrogen bonds, there are π–π ring stacking interactions involving the pyrimidine and pyrazine rings [centroid–centroid distance = 3.689 (1)Å], and two different pyrazine rings [centroid–centroid distance = 3.470 (1)Å]. Finally, there is a C—O$\cdots\pi$ contact involving a carboxylate C—O and the pyrimidine ring with a short O$\cdots$*Cg* distance of 2.738 (2) Å.

Related literature

The precursor 6-acetyl-1,3,7-trimethyllumazine (DLMAceM) was obtained according to literature methods, see: Kim *et al.* (1999). For the structural features of both free and complexed related pteridine derivatives, see for example: Jiménez-Pulido *et al.* (2008*a*,*b*, 2009).



Experimental

Crystal data

$C_{10}H_{10}N_4O_4{\cdot}0.5H_2O$
M_r = 259.23
Monoclinic, $C2/c$
a = 15.7328 (19) Å
b = 11.5784 (16) Å
c = 12.4062 (18) Å
β = 106.113 (10)°
V = 2171.1 (5) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.13 mm^{-1}
T = 120 K
0.46 × 0.24 × 0.19 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.944, T_{max} = 0.976
14172 measured reflections
1970 independent reflections
1493 reflections with $I > 2\sigma(I)$
R_{int} = 0.038

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.055
$wR(F^2)$ = 0.140
S = 1.21
1970 reflections
180 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.65 e Å^{-3}
$\Delta\rho_{min}$ = −0.58 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1w—H1w$\cdots$O4^{i}	0.91 (2)	1.94 (2)	2.841 (2)	172 (3)
O1w—H1w$\cdots$N5^{i}	0.91 (2)	2.52 (3)	2.988 (2)	113 (2)
O61—H61$\cdots$O1w	0.99 (3)	1.87 (3)	2.774 (2)	151 (3)
O61—H61$\cdots$N5	0.99 (3)	2.13 (4)	2.635 (2)	110 (2)

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

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DIRAX/LSQ* (Duisenberg, 1992); data reduction: *EVALCCD* (Duisenberg *et al.*, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON* (Spek, 2009).

Thanks are due to the Plan de Apoyo a la Investigación, al Desarrollo Tecnológico y a la Innovación de la Universidad de Jaén (RFC PP2008 UJA 08 16 08) and the Junta de Andalucía (FQM-273) for financial support.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BG2332).

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Acta Cryst. (2010). E**66**, o719–o720 [doi:10.1107/S1600536810007166]

1,3,7-Trimethyl-2,4-dioxo-1,2,3,4-tetrahydropteridine-6-carboxylic acid hemihydrate

René Faure, Nuria A. Illán-Cabeza, Sonia B. Jiménez-Pulido, Fátima M. Linares-Ordóñez and Miguel N. Moreno-Carretero

S1. Comment

The interest in the 6-substituted lumazine derivatives has been increased since new coordination position pathways and new chemical and biological properties are provided while keeping the similarity to natural pterines. In this article we describe a new pteridine derivative, the 6-carboxy-1,3,7-trimetillumazine (6-carboxy-1,3,7-trimethyl-pteridine-2,4(1*H*,3H)-dione), which crystallizes as hemihydrate. The two rings of the pteridine system are nearly coplanar (acute dihedral angle 4.25°). The atoms of carboxylic group are also coplanar with the pteridine moiety. The presence of the water molecule makes the hydrogen bond pattern different from the usual one in many carboxylic acid compounds: in the present structure the water molecule, which lies on a binary axis, acts like a bridge between two molecules, using its full ability for H-bond formation (Fig. 1, Table 1). In addition to the H-bonds, there are π-π ring stacking interactions which involves the pirimidine (x,y,z) and pyrazine (1/2-x, 3/2-y,-z) rings (Fig. 2). The perpendicular distances are 3.261 and 3.173 Å, the centroid-centroid separation is 3.689 Å, the dihedral angle between the planes concerned is 4.25 °. Another π-π interaction between the pyrazine ring portions at (x,y,z) and (1/2-x,3/2-y,-z) is observed. The parameters, in the same order as before mentioned, are 3.189 Å, 3.470 Å, 0.02 °, respectively, corresponding to a centroids offset of 1.368 Å. Also, there is an important C—O···π contact involving O62 and the pyrimidine ring in x, 1-y, z-1/2 with a distance between the O62 atom and the centroid of the ring of 2.738 (2) Å, a slipping angle between the O62-centroid vector and the normal to the ring of 11.4° and a C61—O62···centroid angle of 131.2 (1)° .

S2. Experimental

The new carboxylate ligand was prepared from the oxidation of 6-acetyl-1,3,7-trimethyllumazine with HNO_3 (40%). This suspension was stirred at room temperature for 3 hours. The ligand was filtered off and isolated in high yield (75-80%). The pale-yellow solution was kept at room for several days, affording prismatic yellow crystals that were collected and used for X-ray diffraction studies.

(6-acetyl-1,3,7-trimethyllumazine (DLMAceM) was prepared by standard Timmis reaction between 6-amino-5-nitrosopyrimidines and 1,3-dicarbonylic derivatives by the method described by Kim *et al.*)

S3. Refinement

The H atoms attached to O61 and O1w were located in subsequents difference Fourier map and refined isotropically. Methyl hydrogens were fixed geometrically and treated as riding with U_{iso}=1.5U_{eq}(C).

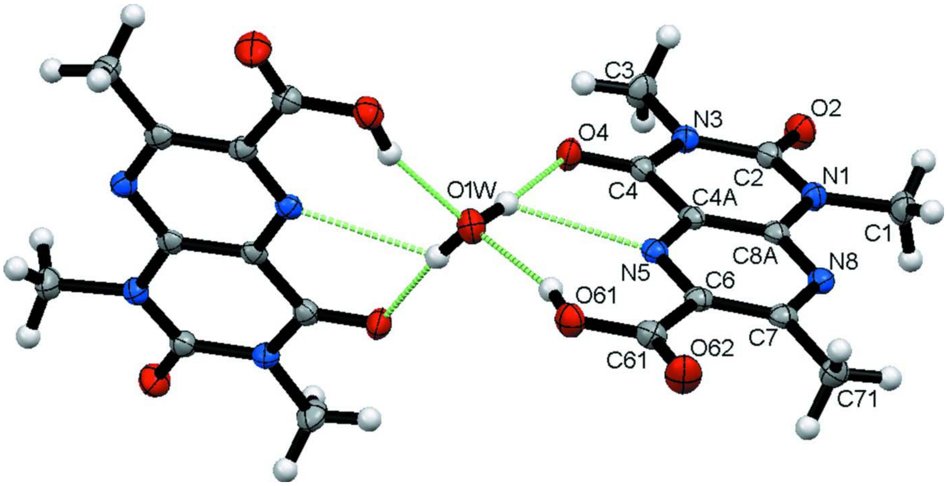

Figure 1

View of the H-bonds (light green broken lines) scheme for 6-carboxy-1,3,7-trimethyllumazine showing the atom labels. Thermal ellipsoids are drawn at the 50% probability level.

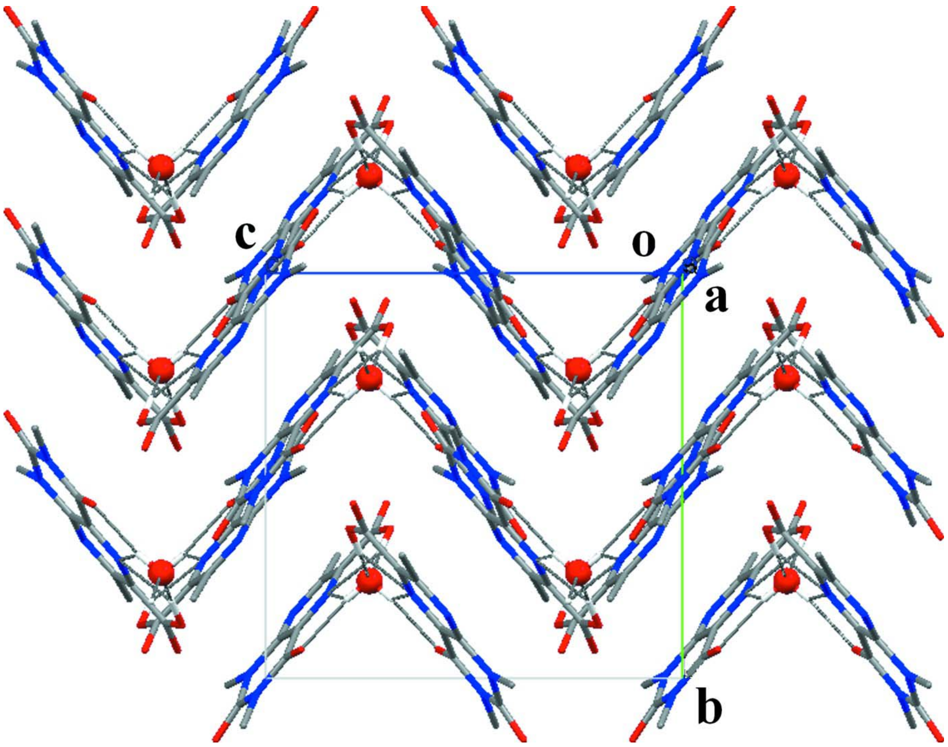

Figure 2

View along [100] of the molecular arrangement in the crystal.

1,3,7-Trimethyl-2,4-dioxo-1,2,3,4-tetrahydropteridine-6-carboxylic acid hemihydrate

Crystal data

$C_{10}H_{10}N_4O_4 \cdot 0.5H_2O$
$M_r = 259.23$
Monoclinic, $C2/c$

Hall symbol: -C 2yc
$a = 15.7328\ (19)$ Å
$b = 11.5784\ (16)$ Å

c = 12.4062 (18) Å
β = 106.113 (10)°
V = 2171.1 (5) Å^3
Z = 8
F(000) = 1080
D_x = 1.586 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 1970 reflections
θ = 2.2–25.3°
μ = 0.13 mm^{-1}
T = 120 K
Prism, light yellow
0.46 × 0.24 × 0.19 mm

Data collection

Nonius KappaCCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
CCD rotation images, thick slices scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.944, T_{max} = 0.976
14172 measured reflections
1970 independent reflections
1493 reflections with $I > 2\sigma(I)$
R_{int} = 0.038
θ_{max} = 25.3°, θ_{min} = 2.2°
h = −18→18
k = −13→13
l = −14→14

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.055
$wR(F^2)$ = 0.140
S = 1.21
1970 reflections
180 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0794P)^2 + 0.6244P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ < 0.001
$\Delta\rho_{max}$ = 0.65 e Å^{-3}
$\Delta\rho_{min}$ = −0.58 e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0125 (14)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of *F*^2^ against ALL reflections. The weighted *R*-factor wR and goodness of fit *S* are based on *F*^2^, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative *F*^2^. The threshold expression of *F*^2^ > *σ*(*F*^2^) is used only for calculating *R*-factors(gt) etc. and is not relevant to the choice of reflections for refinement. *R*-factors based on *F*^2^ are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
O1w	0.5000	0.75980 (19)	0.2500	0.0271 (5)
N1	0.16439 (11)	0.99057 (14)	−0.04043 (14)	0.0213 (4)
C2	0.22500 (13)	1.06607 (18)	−0.06308 (17)	0.0217 (5)
N3	0.31401 (11)	1.03800 (14)	−0.02157 (14)	0.0215 (4)
C4	0.34674 (13)	0.94797 (17)	0.04960 (16)	0.0201 (5)
C4A	0.27938 (13)	0.87743 (17)	0.07728 (15)	0.0181 (5)
N5	0.30569 (11)	0.79181 (13)	0.14868 (13)	0.0190 (4)

C6	0.24465 (13)	0.73144 (16)	0.17889 (16)	0.0201 (5)
C7	0.15435 (14)	0.75701 (17)	0.13777 (16)	0.0211 (5)
N8	0.12794 (11)	0.84253 (14)	0.06406 (13)	0.0209 (4)
C8A	0.18987 (13)	0.90176 (17)	0.03424 (15)	0.0189 (5)
C1	0.07098 (14)	1.0169 (2)	−0.09039 (18)	0.0294 (6)
O2	0.20238 (10)	1.15152 (13)	−0.11888 (12)	0.0303 (4)
C3	0.37550 (14)	1.11665 (19)	−0.05308 (19)	0.0289 (5)
O4	0.42558 (9)	0.92948 (12)	0.08549 (12)	0.0257 (4)
C61	0.28018 (14)	0.63747 (18)	0.26029 (17)	0.0246 (5)
O61	0.36742 (10)	0.63064 (13)	0.30013 (12)	0.0283 (4)
O62	0.23356 (10)	0.56896 (13)	0.28942 (13)	0.0362 (5)
C71	0.08347 (14)	0.69621 (18)	0.17313 (18)	0.0267 (5)
H1W	0.5284 (19)	0.809 (2)	0.305 (2)	0.065 (10)*
H1A	0.0366	0.9451	−0.1014	0.044*
H1B	0.0636	1.0550	−0.1630	0.044*
H1C	0.0501	1.0683	−0.0404	0.044*
H3A	0.4363	1.0901	−0.0197	0.043*
H3B	0.3684	1.1945	−0.0257	0.043*
H3C	0.3631	1.1182	−0.1350	0.043*
H61	0.398 (2)	0.694 (3)	0.273 (3)	0.068 (9)*
H71A	0.0264	0.7330	0.1379	0.040*
H71B	0.0958	0.7004	0.2549	0.040*
H71C	0.0814	0.6151	0.1499	0.040*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1w	0.0226 (11)	0.0273 (12)	0.0279 (12)	0.000	0.0013 (9)	0.000
N1	0.0182 (9)	0.0239 (9)	0.0210 (9)	0.0019 (7)	0.0040 (7)	0.0038 (7)
C2	0.0226 (11)	0.0241 (11)	0.0182 (10)	0.0020 (9)	0.0055 (8)	−0.0001 (9)
N3	0.0204 (9)	0.0235 (9)	0.0206 (9)	−0.0005 (7)	0.0059 (7)	0.0031 (7)
C4	0.0211 (11)	0.0217 (11)	0.0167 (10)	0.0000 (9)	0.0036 (8)	−0.0015 (8)
C4A	0.0205 (11)	0.0188 (10)	0.0153 (10)	0.0026 (8)	0.0056 (8)	−0.0013 (8)
N5	0.0212 (9)	0.0189 (9)	0.0168 (8)	0.0006 (7)	0.0053 (7)	−0.0021 (7)
C6	0.0230 (11)	0.0201 (11)	0.0181 (10)	−0.0025 (9)	0.0073 (8)	−0.0029 (8)
C7	0.0251 (11)	0.0213 (11)	0.0178 (10)	−0.0019 (9)	0.0073 (9)	−0.0048 (8)
N8	0.0198 (9)	0.0228 (9)	0.0208 (9)	−0.0002 (7)	0.0067 (7)	−0.0017 (7)
C8A	0.0216 (11)	0.0199 (11)	0.0152 (10)	0.0009 (8)	0.0053 (8)	−0.0040 (8)
C1	0.0193 (11)	0.0373 (13)	0.0296 (12)	0.0047 (10)	0.0037 (9)	0.0078 (10)
O2	0.0283 (9)	0.0298 (9)	0.0318 (9)	0.0052 (7)	0.0065 (7)	0.0114 (7)
C3	0.0242 (12)	0.0299 (12)	0.0332 (12)	−0.0037 (10)	0.0091 (10)	0.0082 (10)
O4	0.0168 (8)	0.0304 (8)	0.0288 (8)	0.0000 (6)	0.0047 (6)	0.0050 (6)
C61	0.0276 (12)	0.0251 (12)	0.0209 (11)	−0.0005 (9)	0.0064 (9)	0.0003 (9)
O61	0.0265 (8)	0.0282 (9)	0.0277 (8)	0.0026 (7)	0.0036 (7)	0.0056 (7)
O62	0.0352 (9)	0.0340 (9)	0.0391 (10)	−0.0040 (8)	0.0100 (8)	0.0148 (8)
C71	0.0234 (11)	0.0314 (12)	0.0265 (12)	−0.0048 (10)	0.0093 (9)	−0.0009 (9)

Geometric parameters (Å, º)

O1w—H1W	0.90 (3)	N1—C2	1.379 (3)
O4—C4	1.215 (2)	N1—C1	1.460 (3)
C4A—N5	1.317 (3)	O61—C61	1.326 (3)
C4A—C8A	1.389 (3)	O61—H61	0.98 (3)
C4A—C4	1.453 (3)	O62—C61	1.202 (3)
N8—C8A	1.325 (3)	C7—C71	1.484 (3)
N8—C7	1.334 (3)	C71—H71A	0.9800
N5—C6	1.323 (3)	C71—H71B	0.9800
N3—C4	1.371 (3)	C71—H71C	0.9800
N3—C2	1.390 (3)	C3—H3A	0.9800
N3—C3	1.459 (3)	C3—H3B	0.9800
O2—C2	1.203 (2)	C3—H3C	0.9800
C8A—N1	1.367 (3)	C1—H1A	0.9800
C6—C7	1.401 (3)	C1—H1B	0.9800
C6—C61	1.484 (3)	C1—H1C	0.9800

N5—C4A—C8A	120.46 (18)	O2—C2—N1	121.85 (19)
N5—C4A—C4	117.93 (18)	O2—C2—N3	120.80 (18)
C8A—C4A—C4	121.56 (18)	N1—C2—N3	117.32 (17)
C8A—N8—C7	117.54 (18)	C7—C71—H71A	109.5
C4A—N5—C6	118.07 (18)	C7—C71—H71B	109.5
C4—N3—C2	125.18 (17)	H71A—C71—H71B	109.5
C4—N3—C3	119.27 (17)	C7—C71—H71C	109.5
C2—N3—C3	115.45 (16)	H71A—C71—H71C	109.5
N8—C8A—N1	118.56 (18)	H71B—C71—H71C	109.5
N8—C8A—C4A	122.21 (18)	N3—C3—H3A	109.5
N1—C8A—C4A	119.22 (18)	N3—C3—H3B	109.5
N5—C6—C7	121.83 (18)	H3A—C3—H3B	109.5
N5—C6—C61	114.46 (18)	N3—C3—H3C	109.5
C7—C6—C61	123.70 (18)	H3A—C3—H3C	109.5
C8A—N1—C2	121.70 (17)	H3B—C3—H3C	109.5
C8A—N1—C1	121.06 (17)	O62—C61—O61	120.23 (19)
C2—N1—C1	116.92 (17)	O62—C61—C6	122.8 (2)
C61—O61—H61	112.3 (17)	O61—C61—C6	116.92 (18)
O4—C4—N3	122.20 (18)	N1—C1—H1A	109.5
O4—C4—C4A	123.50 (18)	N1—C1—H1B	109.5
N3—C4—C4A	114.30 (17)	H1A—C1—H1B	109.5
N8—C7—C6	119.86 (18)	N1—C1—H1C	109.5
N8—C7—C71	115.99 (19)	H1A—C1—H1C	109.5
C6—C7—C71	124.13 (18)	H1B—C1—H1C	109.5

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*w*—H1w···O4^{i}	0.91 (2)	1.94 (2)	2.841 (2)	172 (3)
O1*w*—H1w···N5^{i}	0.91 (2)	2.52 (3)	2.988 (2)	113 (2)

O61—H61···O1*w*	0.99 (3)	1.87 (3)	2.774 (2)	151 (3)
O61—H61···N5	0.99 (3)	2.13 (4)	2.635 (2)	110 (2)

Symmetry code: (i) −*x*+1, *y*, −*z*+1/2.