

N-(3-Methyl-4-oxo-3,4-dihydropteridin-2-yl)glycine: hydrogen-bonded sheets of $R_4^4(22)$ and $R_4^4(30)$ rings

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Molecules of the title compound, $C_9H_9N_5O_3$, are linked into sheets by a combination of one $O-H\cdots N$ hydrogen bond and one $N-H\cdots O$ hydrogen bond.

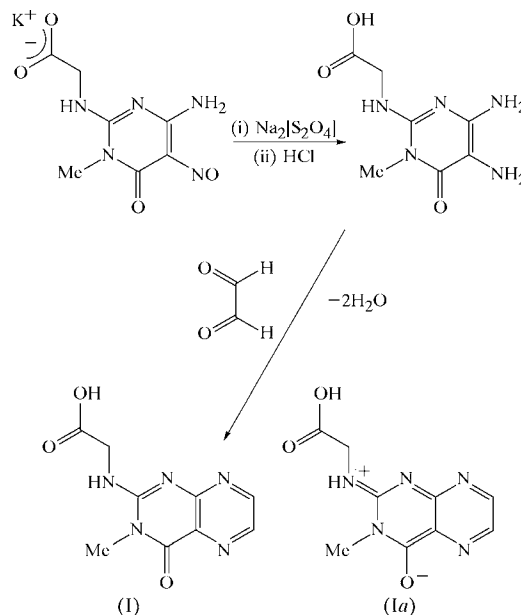
Comment

The title compound, (I), is of potential biological interest, since it is an *N*-pteridinyl derivative of the amino acid glycine. Compounds of this general type can be adsorbed on activated carbon, implying π - π interactions between the heteroaromatic moiety and the carbon surface (Coughlin & Ezra, 1968; Mattson *et al.*, 1969; Leon y Leon *et al.*, 1992; Radovic *et al.*, 1997), while the carboxyl function remains available in the solvent phase to act as a coordinating site for metal ions in solution, thus providing the basis of a possible method for the removal of toxic metal ions from waste water.

The bond distances within the molecule of (I) present some unexpected values (Table 1), which are not readily reconciled with the classically localized bond-valence form. In particular, the C6—C7 and C4a—C8a bonds, which are formally single and double bonds, respectively, have effectively identical lengths. In addition, the C2—N2 bond, which is formally a single bond, is barely longer than the N5—C6 and C7—N8 bonds, which are formally double bonds. On the other hand, these latter two are significantly shorter than any of C4a—N5, N8—C8a and C8a—N1. These observations render somewhat problematical the graphical representation of the molecular-electronic structure. The polarized form (Ia) can be ruled out on the grounds that the N8—C8a and C8a—N1 bonds have effectively identical lengths, and because C4—C4a is by far the longest C—C bond in the ring system. The bond distances in the N3—C4—O4 amidic fragment are normal for their types (Allen *et al.*, 1987). Within the carboxyl group, the C—O

distances are fully consistent with the localization of the H atom as deduced from a difference map.

While the bicyclic portion of the molecule is effectively planar, with a maximum deviation from the best least-squares plane of 0.052 (2) Å for atom N8, the conformation of the glycine side chain (Fig. 1 and Table 1) may well be influenced by the short intramolecular contact involving atoms H21*B* and N1 (Table 2), which generates a nearly planar *S*(5) ring (Bernstein *et al.*, 1995).



The molecules of (I) are linked *via* a combination of $O-H\cdots N$ and $N-H\cdots O$ hydrogen bonds (Table 2) into sheets, within which each of the two hydrogen bonds alone produces a one-dimensional substructure. It is striking that neither of the motifs characteristic of simple carboxylic acids, *viz.* the $C(4)$ chain and the cyclic $R_2^2(8)$ dimer, is present in the structure of (I). In the first substructure, carboxyl atom O21 in the molecule at (x, y, z) acts as hydrogen-bond donor to atom N8 in the molecule at $(\frac{1}{2} + x, \frac{1}{2} - y, 1 - z)$, so forming a $C(9)$ chain running parallel to the [100] direction and generated by the 2_1

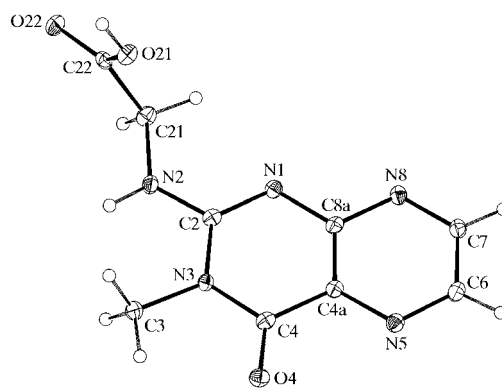


Figure 1
The molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

screw axis along $(x, \frac{1}{4}, \frac{1}{2})$ (Fig. 2). In the second substructure, amino atom N2 in the molecule at (x, y, z) acts as hydrogen-bond donor to carbonyl atom O4 in the molecule at $(\frac{1}{2} - x, y - \frac{1}{2}, z)$, so forming a $C(6)$ chain running parallel to the $[010]$

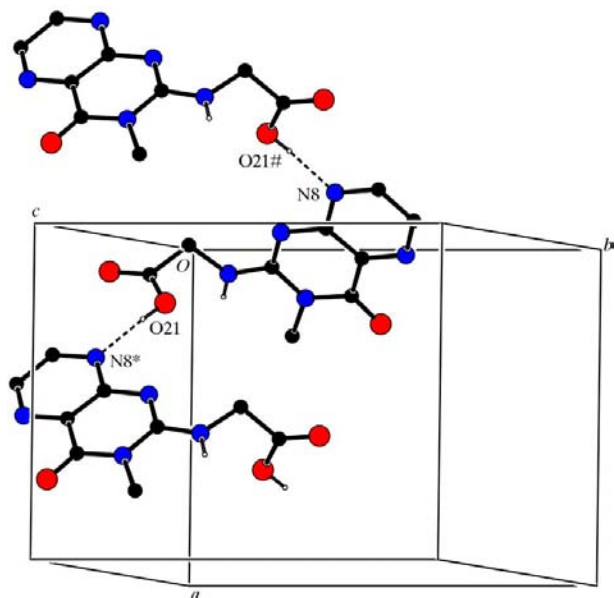


Figure 2
Part of the crystal structure of (I), showing the formation of a $C(9)$ chain along $[100]$. For the sake of clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(\frac{1}{2} + x, \frac{1}{2} - y, 1 - z)$ and $(x - \frac{1}{2}, \frac{1}{2} - y, 1 - z)$, respectively.

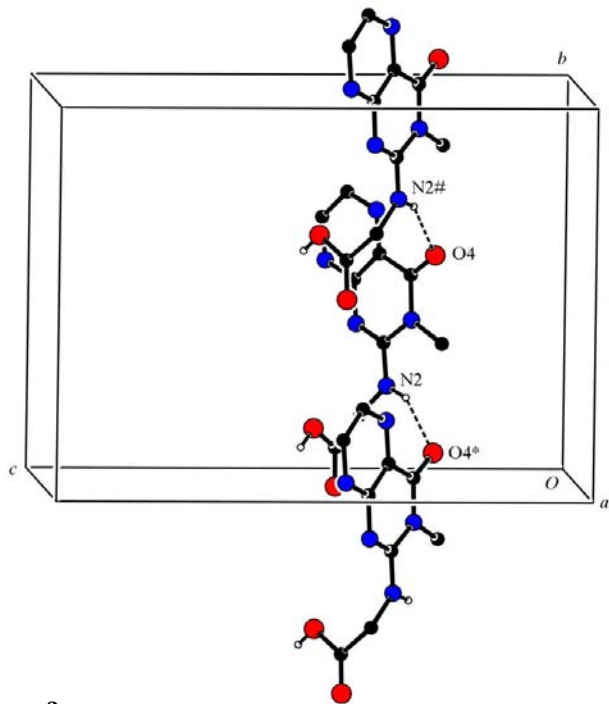


Figure 3
Part of the crystal structure of (I), showing the formation of a $C(6)$ chain along $[010]$. For the sake of clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(\frac{1}{2} - x, y - \frac{1}{2}, z)$ and $(\frac{1}{2} - x, \frac{1}{2} + y, z)$, respectively.

direction and generated by the b -glide plane at $x = \frac{1}{4}$ (Fig. 3). The combination of these chains generates a (001) sheet in the form of a $(4,4)$ -net (Batten & Robson, 1998) built from centrosymmetric $R_4^2(22)$ and $R_4^2(30)$ rings alternating in a chess-board fashion (Fig. 4). Around the periphery of the $R_4^2(30)$ rings, each molecule acts as a single donor and single acceptor of hydrogen bonds, while around the periphery of the $R_4^2(22)$ rings, one pair of centrosymmetrically related molecules act as double donors and the other such pair as double acceptors of hydrogen bonds.

Two of these sheets, related to one another by the 2_1 screw axes parallel to $[001]$, pass through each unit cell, in the domains $0.24 < z < 0.76$ and $0.74 < z < 1.26$, respectively, and the sole direction-specific interaction between adjacent sheets is a π - π stacking interaction between the pyrimidine ring portions of the molecules at (x, y, z) and $(-x, y, \frac{1}{2} - z)$. The planes of these two rings make an angle of only $1.9(2)^\circ$; the interplanar spacing is $3.218(2) \text{ \AA}$ and the centroid-centroid separation is $3.363(2) \text{ \AA}$, corresponding to a centroid offset of $0.977(2) \text{ \AA}$ (Fig. 5). This interaction thus links each (001) sheet to the two neighbouring sheets, so linking all of the sheets into a single three-dimensional aggregate.

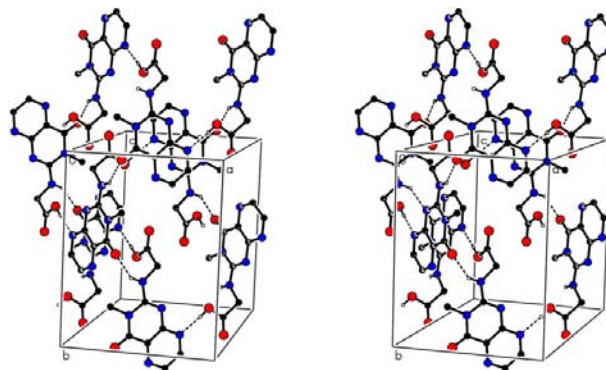


Figure 4
A stereoview of part of the crystal structure of (I), showing the formation of an (001) sheet of alternating $R_4^2(22)$ and $R_4^2(30)$ rings. For the sake of clarity, H atoms bonded to C atoms have been omitted.

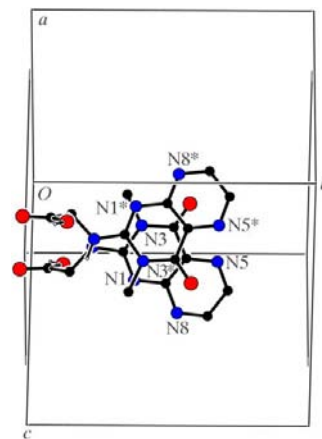


Figure 5
Part of the crystal structure of (I), showing the π - π stacking interaction which links adjacent (001) sheets. For the sake of clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*) are at the symmetry position $(-x, y, \frac{1}{2} - z)$.

Experimental

The title compound was prepared by adding sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$; 10 g, 60 mmol) to an aqueous solution of potassium *N*-(6-amino-3,4-dihydro-3-methyl-5-nitroso-4-oxopyrimidin-2-yl)glycinate (Low *et al.*, 2001; 10 g, 37.7 mmol) at *ca* 340 K. The resulting solution was cooled in an ice bath, and the precipitated solids were filtered off and washed with water and then ethanol. An aqueous solution of the resulting 5,6-diamine (2.0 g, 9.3 mmol) was then heated with glyoxal (2.01 ml of a 40% aqueous solution) under reflux for 1 h. The mixture was adjusted to pH 2–3 using hydrochloric acid and then cooled to give a solid, crystallization of which from 50% (*v/v*) aqueous methanol gave pale-brown crystals of (I) suitable for single-crystal X-ray diffraction analysis.

Crystal data

$\text{C}_9\text{H}_9\text{N}_5\text{O}_3$	Mo $K\alpha$ radiation
$M_r = 235.21$	Cell parameters from 1899 reflections
Orthorhombic, <i>Pbcn</i>	$\theta = 3.4\text{--}26.0^\circ$
$a = 9.6497(7) \text{ \AA}$	$\mu = 0.13 \text{ mm}^{-1}$
$b = 12.1378(5) \text{ \AA}$	$T = 120(2) \text{ K}$
$c = 16.5063(11) \text{ \AA}$	Plate, pale brown
$V = 1933.3(2) \text{ \AA}^3$	$0.16 \times 0.14 \times 0.03 \text{ mm}$
$Z = 8$	
$D_x = 1.616 \text{ Mg m}^{-3}$	

Data collection

Nonius KappaCCD area-detector diffractometer	1899 independent reflections
φ and ω scans	1347 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	$R_{\text{int}} = 0.095$
$T_{\text{min}} = 0.974$, $T_{\text{max}} = 0.996$	$\theta_{\text{max}} = 26.0^\circ$
13 945 measured reflections	$h = -11 \rightarrow 11$
	$k = -14 \rightarrow 14$
	$l = -20 \rightarrow 17$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0312P)^2 + 1.3421P]$
$R[F^2 > 2\sigma(F^2)] = 0.070$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.106$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.08$	$\Delta\rho_{\text{max}} = 0.22 \text{ e \AA}^{-3}$
1899 reflections	$\Delta\rho_{\text{min}} = -0.22 \text{ e \AA}^{-3}$
156 parameters	
H-atom parameters constrained	

Table 1

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

N1—C2	1.314 (3)	N8—C8a	1.360 (3)
C2—N3	1.397 (3)	C8a—N1	1.362 (3)
N3—C4	1.382 (3)	C4a—C8a	1.396 (3)
C4—C4a	1.459 (3)	C2—N2	1.333 (3)
C4a—N5	1.345 (3)	C4—O4	1.234 (3)
N5—C6	1.324 (3)	C22—O21	1.326 (3)
C6—C7	1.398 (3)	C22—O22	1.210 (3)
C7—N8	1.326 (3)		
N1—C2—N2—C21	−1.9 (3)	N2—C21—C22—O21	51.0 (3)
C2—N2—C21—C22	−124.3 (2)	N2—C21—C22—O22	−129.6 (2)

Space group *Pbcn* was uniquely assigned from the systematic absences. All H atoms were located from difference maps and

Table 2

Geometry of hydrogen bonds and short intramolecular contacts (\AA , $^\circ$).

$D\text{—}H\cdots A$	$D\text{—}H$	$H\cdots A$	$D\cdots A$	$D\text{—}H\cdots A$
O21—H21 \cdots N8 ⁱ	0.84	1.86	2.697 (3)	177
N2—H2 \cdots O4 ⁱⁱ	0.88	2.00	2.773 (3)	146
C21—H21B \cdots N1	0.99	2.37	2.799 (3)	105

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

subsequently treated as riding atoms, with C—H = 0.95 (aromatic), 0.98 (CH_3) or 0.99 \AA (CH_2), N—H = 0.88 \AA and O—H = 0.84 \AA , and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$, $1.5U_{\text{eq}}(\text{C})$ for methyl H, and $1.5U_{\text{eq}}(\text{O})$.

Data collection: COLLECT (Hooft, 1999); cell refinement: DENZO (Otwinowski & Minor, 1997) and COLLECT; data reduction: DENZO and COLLECT; program(s) used to solve structure: OSCAIL (McArdle, 2003) and SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: OSCAIL and SHELXL97 (Sheldrick, 1997); molecular graphics: PLATON (Spek, 2003); software used to prepare material for publication: SHELXL97 and PRPKAPPA (Ferguson, 1999).

The X-ray data were collected at the EPSRC X-ray Crystallographic Service, University of Southampton, England; the authors thank the staff for all their help and advice. JNL thanks NCR Self-Service, Dundee, for grants which have provided computing facilities for this work.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1769). Services for accessing these data are described at the back of the journal.

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