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The supramolecular structure of *N*-(6-amino-3,4-dihydro-3-methyl-5-nitroso-4-oxopyrimidin-2-yl)glycylglycinate contains a unique O—H···N(nitroso) hydrogen bond

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Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.002 Å
R factor = 0.044
wR factor = 0.122
Data-to-parameter ratio = 12.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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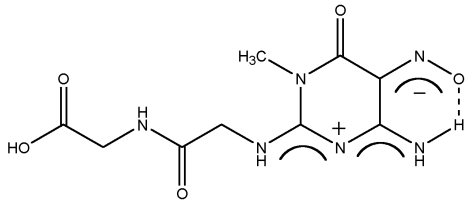
The molecular structure of the title compound, $C_9H_{12}N_6O_5$, shows extensive electronic delocalization involving the pyrimidine ring and the attached N atom of the glycylglycinate, the amino and the nitroso groups. A unique O—H···N(nitroso) hydrogen bond of 2.748 (2) Å is found in the structure. The supramolecular structure is a three-dimensional network, derived from two sets of antiparallel chains, which link chains of alternating dimers which are formed by the action of two different crystallographic centres of symmetry.

Comment

Table 1 gives selected bond lengths for the title compound, (I), and these indicate that the structure of the pyrimidine moiety shows the same delocalization as reported by Low *et al.* (2000), as shown in the Scheme. The torsion angles along the glycylglycinate side chain are also listed. These angles are ultimately defined by the hydrogen bonding within the supramolecular structure since the three donor atoms in this side chain (N21, N22 and O22), along with the amino nitrogen (N6) play a major part in the formation of the supramolecular structure. In the K (Low, Arranz, Cobo, Fontecha, Godino, López & Glidewell, 2001) and Ca (Low, Arranz, Cobo, Fontecha, Godino, López, Cannon *et al.*, 2001) complexes, the torsion angle N21—C21—C22—N22, which determines the orientation of the side chain, has values of 15.1 (2) and −0.5 (4)°, respectively, compared with 75.3 (2)° in (I), an indication of how different environments can affect the orientation of these chains.



(I)

In all the structures reported in Low *et al.* (2000), there was a very short hydrogen bond, around 2.44–2.50 Å, between the hydroxyl H atom of the carboxylate group of the amino acid side chain and the O atom of the nitroso group, but no hydrogen bond involving the N atom of the nitroso group. In (I), there is no short O···O hydrogen bond, but rather the hydroxyl H atom bonds to the N atom of the nitroso group. This type of hydrogen bond is unique in the literature. A search was made of the Cambridge Structural Database (April 2002 Release; Allen & Kennard, 1993), for any organic hydroxyl hydrogen bond contact to any organic nitroso group and no possible hydrogen-bond contacts were found involving

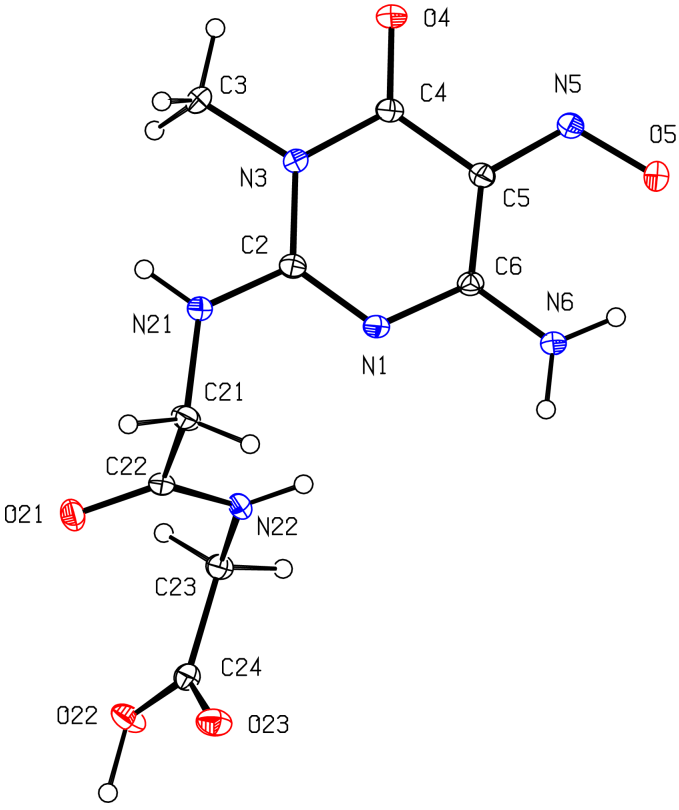


Figure 1
A view of (I) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

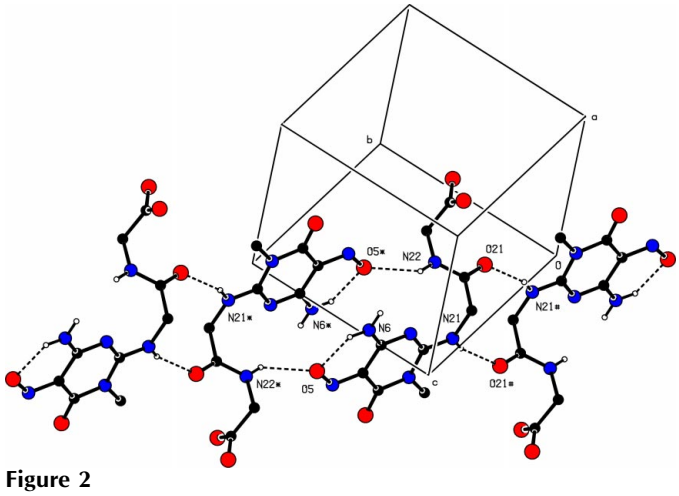


Figure 2
A view of the crystal structure of (I), showing the dimer chains. All H atoms attached to C atoms have been omitted. Atoms labelled with an asterisk (*) and hash (#) are in molecules at positions $(-x, 1-y, 2-z)$ and $(-x, -y, 1-z)$, respectively.

the N atom. In addition, a search was made for any hydroxyl group interacting with any sp^2 N atom attached to a C and any other atom. 719 hits were obtained for O···N contacts in the range 2.465–3.134 Å, with an angle at hydrogen of greater than 130°. The median value for the O···N distance for this sample was 2.668 Å, which is close to the distance of 2.748 (2) Å found for (I).

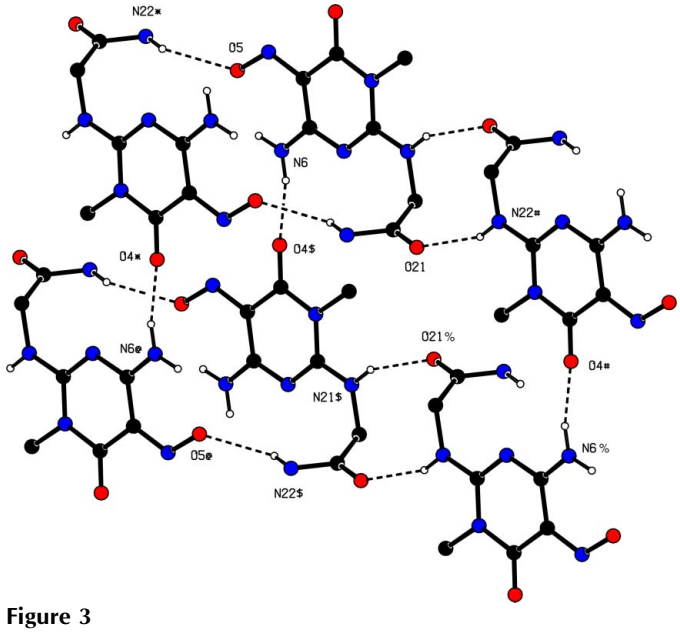


Figure 3
A view of the crystal structure of (I), showing the rings formed in the sheets which lie in $(0\bar{1}1)$. The glycinate side chain and the unit-cell box and all H atoms attached to C atoms have been omitted for the sake of clarity. Atoms labelled with an asterisk (*), hash (#), dollar sign ($), percentage sign (%) and 'at' symbol (@) are in molecules at positions $(-x, 1-y, 2-z)$, $(-x, -y, 1-z)$, $(1+x, y, z)$, $(1-x, -y, 1-z)$ and $(1-x, 1-y, 2-z)$, respectively.

In (I), the nitroso O atom acts as an acceptor for the H atom of the amide group of the glycylglycinate side chain. Table 2 lists the hydrogen bonds present in the structure.

The N6—H6*B*···O5 intramolecular hydrogen bond forms an *S*(6) ring (Bernstein *et al.*, 1995); this is found in the analogous structures described in Low *et al.* (2000).

The N22—H22*A*···O5^{iii} and N21—H21···O21^{ii} hydrogen bonds (see Table 2 for symmetry codes) link the molecules into $C_2^2(16)$ chains (Bernstein *et al.*, 1995), running parallel to [011]. The action of crystallographic centres of symmetry produce an antiparallel chain. The former bond through the action of the centre-of-symmetry at (0, 0.5, 1) forms an $R_2^2(22)$ ring, whilst the latter bond, through the action of the centre of symmetry (0, 0, 0.5), forms an $R_2^2(10)$ ring, thus forming a chain of alternating dimers (Fig. 2).

The N6—H6*A*···O4^{iv} hydrogen bond links the molecules into a *C*(8) chain running parallel to [100]. Crystallographic centres-of-symmetry produce a series of alternating anti-parallel chains. These link the dimer chains together forming two-layered sheets which lie in $(0\bar{1}1)$ and which consist of a series of ring structures (Fig. 3). There are several possible ring structures but only two of them are described here. The first involves the N22—H22*A*···O5 and N6—H6*A*···O4 hydrogen bonds and is an $R_4^4(32)$ ring in which N6 acts as a donor to O4$(1+x, y, z)$, N22$(1+x, y, z)$ acts as a donor to O5$(1-x, 1-y, 2-z)$, N6$(1-x, 1-y, 2-z)$ acts as a donor to O4$(-x, 1-y, 2-z)$ and finally N22$(-x, 1-y, 2-z)$ acts as a donor to O5(x, y, z). The second involves the N21—H21···O21 and N6—H6*A*···O4 hydrogen bonds in an $R_4^4(30)$ ring in which N6 acts as a donor to O4$(1+x, y, z)$, N21$(1+x,$

y, *z*) acts as a donor to O21($1-x$, $-y$, $1-z$), N6($1-x$, $-y$, $1-z$) acts as a donor to O4($-x$, $-y$, $1-z$) and N21($-x$, $-y$, $1-z$) acts as a donor to O21(*x*, *y*, *z*).

These sheets are then interlinked by a series of antiparallel $C(12)$ chains formed by the O22—H222···N5^{i} hydrogen bond which effectively join the chains of dimers to each other (Fig. 4). As can be seen, this forms two further ring structures, one an $R_4^4(16)$ ring in which N22 acts as a donor to O5($-x$, $1-y$, $2-z$), N5($-x$, $1-y$, $2-z$) acts as an acceptor for O22($1-x$, $1-y$, $1-z$), N22($1-x$, $1-y$, $1-z$) acts as a donor to O5($1+x$, *y*, $-1+z$) and N5($1+x$, *y*, $-1+z$) acts as an acceptor from O22(*x*, *y*, *z*). The other is an $R_4^4(28)$ ring in which O22 acts as a donor to N5($1+x$, *y*, $-1+z$), N21($1+x$, *y*, $-1+z$) acts as a donor to O21($1-x$, $-y$, $-z$), O22($1-x$, $-y$, $-z$) acts as a donor to N5($-x$, $-y$, $1-z$) and N21($-x$, $-y$, $1-z$) acts as a donor to O21(*x*, *y*, *z*).

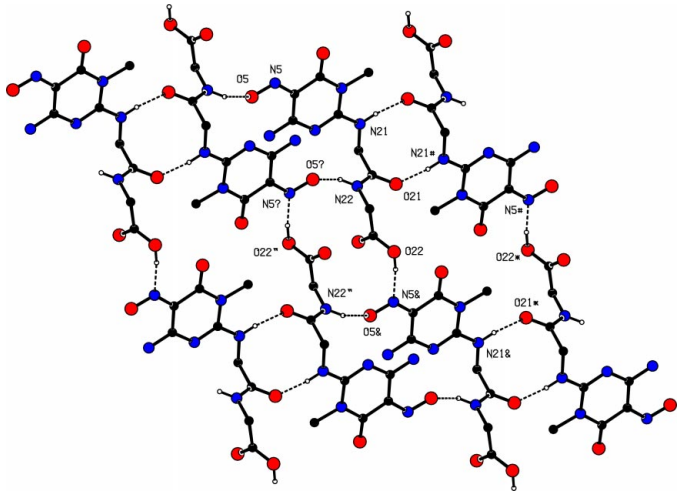


Figure 4
A view of the crystal structure of (I), showing the ring structures which link the ($0\bar{1}1$) sheets together. The unit-cell box and all H atoms attached to C atoms have been omitted for the sake of clarity. Atoms labelled an asterisk (*), hash (#), question mark (?), ampersand (&) and double quotes (") are in molecules at positions ($1+x$, $-y$, $-z$), ($-x$, $-y$, $1-z$), ($-x$, $1-y$, $2-z$), ($1+x$, *y*, $-1+z$) and ($1-x$, $1-y$, $1-z$), respectively.

Experimental

2.14 g (0.016 mol) of glycylglycine dissolved in 16 ml of potassium hydroxide (1 *M*) was added to 6-amino-3,4-dihydro-3-methyl-2-methoxy-5-nitroso-4-oxo-pyrimidine dissolved in 50 ml of acetonitrile. The mixture was heated to reflux at 343 K for 90 min. A purple solid was precipitated. This was filtered off, washed with ethanol and diethyl ether. It was then dissolved in 50 ml of water, to which hydrochloric acid (1 *N*) was added, to obtain a pH of 3 at which point the title compound was precipitated. This was collected by filtration, washed with water, ethanol and diethyl ether. Samples suitable for X-ray diffraction were obtained by recrystallization from water (yield: 88%). Elemental analysis for $C_9H_{12}N_6O_5$, calculated: C 38.03, H 4.25, N 29.57%; found: C 37.81, H 4.35, N 28.97%

Crystal data

$C_9H_{12}N_6O_5$
M_r = 284.25
Triclinic, $P\bar{1}$
a = 7.4727 (6) Å
b = 8.2356 (4) Å
c = 9.6678 (8) Å
α = 81.208 (5)°
β = 88.722 (3)°
γ = 76.169 (4)°
V = 570.87 (7) Å^3
Z = 2
D_x = 1.654 Mg m^{-3}
Mo Kα radiation
Cell parameters from 2321 reflections
θ = 2.8–26.4°
μ = 0.14 mm^{-1}
T = 150 (1) K
Lath, pink
0.30 × 0.10 × 0.05 mm

Data collection

Nonius KappaCCD diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: none
9202 measured reflections
2321 independent reflections
1775 reflections with $I > 2\sigma(I)$
R_{int} = 0.055
θ_{max} = 26.4°
$h = -9 \rightarrow 9$
$k = -10 \rightarrow 10$
$l = -12 \rightarrow 12$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.122
S = 1.03
2321 reflections
182 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0708P)^2 + 0.0612P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.29 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N1—C2	1.329 (2)	C4—C5	1.452 (2)
N1—C6	1.344 (2)	C5—N5	1.340 (2)
C2—N21	1.329 (2)	C5—C6	1.442 (2)
C2—N3	1.380 (2)	N5—O5	1.2811 (18)
N3—C4	1.392 (2)	C6—N6	1.320 (2)
N1—C2—N21—C21	2.5 (2)	C21—C22—N22—C23	−178.48 (14)
N3—C2—N21—C21	−176.41 (14)	C24—C23—N22—C22	−66.09 (19)
C2—N21—C21—C22	−96.96 (18)	N22—C23—C24—O23	−28.4 (2)
N21—C21—C22—O21	−103.45 (18)	N22—C23—C24—O22	153.69 (14)
N21—C21—C22—N22	75.27 (19)	N21—C2—N3—C4	−179.17 (14)
O21—C22—N22—C23	0.2 (2)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O22—H22*B*···N5^{i}	1.05	1.72	2.748 (2)	168
N21—H21···O21^{ii}	0.88	1.96	2.755 (2)	149
N22—H22*A*···N1	0.88	2.64	3.300 (2)	133
N22—H22*A*···O5^{iii}	0.88	2.26	2.940 (2)	135
N6—H6*A*···O4^{iv}	0.88	1.99	2.840 (2)	163
N6—H6*B*···O5	0.88	1.99	2.638 (2)	129

Symmetry codes: (i) $1+x, y, z-1$; (ii) $-x, -y, 1-z$; (iii) $-x, 1-y, 2-z$; (iv) $1+x, y, z$.

H atoms were treated as riding atoms, with C—H = 0.98–0.99 Å, N—H = 0.88 Å and O—H = 1.05 Å. The latter H-atom position was based on the position obtained from a difference map. The methyl group was allowed to rotate but not to tip.

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure:

*SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976) and *PLATON* (Spek, 2002); software used to prepare material for publication: *SHELXL*97 and *WordPerfect* macro *PRPKAPPA* (Ferguson, 1999).

X-ray data were collected at the EPSRC, X-ray Crystallographic Service, University of Southampton, using an Enraf—Nonius KappaCCD diffractometer; 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.

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