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Ethyl *N*-(2-benzylamino-6-benzyloxy-5-nitrosopyrimidin-4-yl)glycinate: sheets built from a three-centre N—H···(N,O), and two-centre C—H···O and C—H···π(arene) hydrogen bonds

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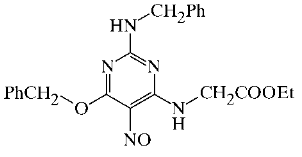
In the title compound, $C_{22}H_{23}N_5O_4$, the molecules are linked into chains by a three-centre N—H···(N,O) hydrogen bond, reinforced by a two-centre C—H···O hydrogen bond, and the chains are further linked into sheets by a combination of C—H···O and C—H···π(arene) hydrogen bonds.

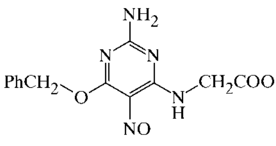
Comment

We report here the molecular and supramolecular structure of the title compound, ethyl *N*-(2-benzylamino-6-benzyloxy-5-nitrosopyrimidin-4-yl)glycinate, (I) (Fig. 1), which we have studied in order to compare the interplay of the molecular and supramolecular structure in (I) with that in the analogue (II) (Quesada, Marchal *et al.*, 2002; Quesada, Low *et al.*, 2002), which differs from (I) in having an unsubstituted amino N2 atom, *i.e.* no benzyl group, as is present in (I). In (II), the molecules are linked into chains by a combination of a three-centre N—H···(N,O) hydrogen bond and an N—H···π(arene) interaction, involving different N—H bonds of the 2-amino group in the two types of interaction. In (I), with no NH_2 group, a different pattern of supramolecular aggregation must occur.

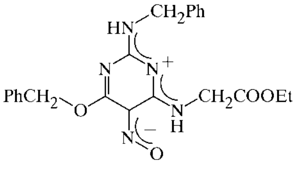
In (I), the amino N4 atom forms the intramolecular N—H···O hydrogen bond typical of 4-amino-5-nitrosopyrimidines (Quesada, Marchal *et al.*, 2002; Quesada, Low *et al.*, 2002) and the amino N2 atom acts as a hydrogen-bond donor to the nitroso atoms N5$^{\rm i}$ and O5$^{\rm i}$ in an almost planar three-centre interaction [symmetry code: (i) $-x, \frac{1}{2}+y, \frac{1}{2}-z$]; propagation of this interaction produces a chain running parallel to the [010] direction and generated by the 2_1 screw axis along $(0, y, \frac{1}{4})$ (Fig. 2). This [010] chain is further reinforced by a C—H···O hydrogen bond, with the nitroso O5 atom again acting as the acceptor (Table 2 and Fig. 2), and the chain thus contains three different ring motifs of $S(6)$, $R^2_1(3)$ and $R^1_2(11)$ types (Bernstein *et al.*, 1995).



(I)



(II)



(I*a*)

Two chains of this type, related to one another by centres of inversion and thus antiparallel, run through each unit cell, generated by the screw axes along $(0, y, \frac{1}{4})$ and $(0, -y, \frac{3}{4})$, and these chains are linked into (100) sheets by a combination of C—H···O and C—H···π(arene) hydrogen bonds (Table 2 and Fig. 3). Atoms C7 (*via* H7*B*) and C22, which are part of the chain along $(0, y, \frac{1}{4})$, both act as hydrogen-bond donors to the carbonyl O81$^{\rm ii}$ atom, which lies in the chain along $(0, -y, \frac{3}{4})$ [symmetry code: (ii) $x, -y+\frac{1}{2}, z+\frac{1}{2}$]. Similarly, atoms C7 and C22 in the molecule at $(-x, \frac{1}{2}+y, \frac{1}{2}-z)$, which also lies in the $(0, y, \frac{1}{4})$ chain, act as donors to O81 in the molecule at $(-x, 1-y, -z)$, which itself lies in the chain along $(0, -y, -\frac{1}{4})$. In this manner, each [010] chain is linked by C—H···O hydrogen bonds to the two neighbouring chains in the [001] direction, so generating a (100) sheet.

The linking of the [010] chains is further reinforced by two distinct C—H···π(arene) interactions. Atoms C7 (*via* H7*A*) and C67 (*via* H67*A*) act as hydrogen-bond donors, respectively, to the centroid *Cg*2$^{\rm ii}$ of ring (C21–C26)$^{\rm ii}$ and to the centroid *Cg*3$^{\rm iii}$ of ring (C61–C66)$^{\rm iii}$ [symmetry code: (iii) $x, \frac{1}{2}-y, z-\frac{1}{2}$]. These two molecules lie in the chains along

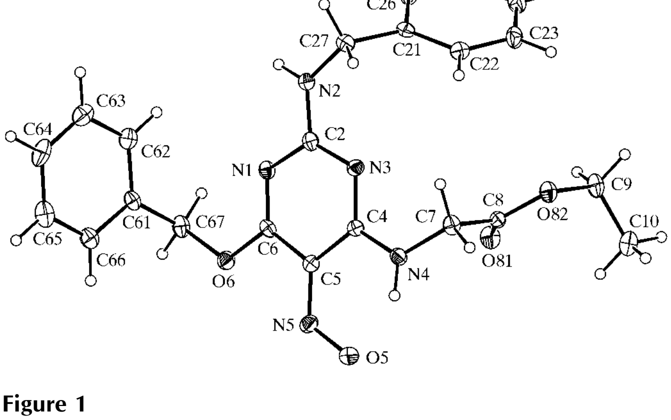


Figure 1
A view of the molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

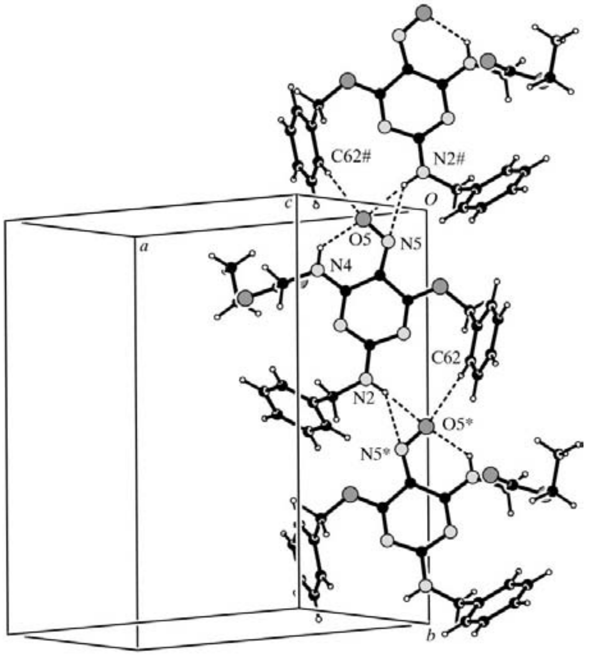


Figure 2
Part of the crystal structure of (I), showing the formation of a chain along [010]. Atoms marked with an asterisk (*) or hash (#) are at the symmetry positions $(-x, \frac{1}{2}+y, \frac{1}{2}-z)$ and $(-x, -\frac{1}{2}+y, \frac{1}{2}-z)$, respectively.

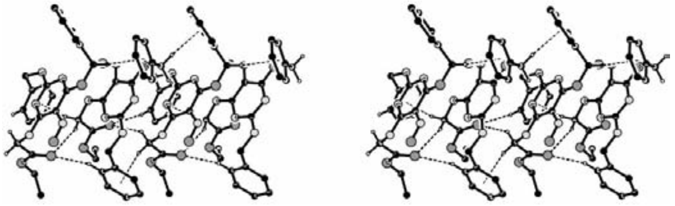


Figure 3
Stereoview of part of the structure of (I), showing the C—H···O and C—H···π(arene) hydrogen bonds which link the [010] chains into a (100) sheet. For the sake of clarity, the unit-cell box has been omitted and only H atoms involved in the motifs shown are included.

$(0, -y, \frac{3}{4})$ and $(0, -y, -\frac{1}{4})$, respectively, and hence these interactions (Fig. 3) reinforce the (100) sheet.

All of the C—H···O and C—H···π(arene) interactions have H···*A* and *D*···*A* distances which are reasonably short for their types, and all except one have *D*—H···*A* angles above 150° (Table 2). However, the co-operative action of the many hydrogen bonds may be more significant than the properties of the individual interactions. It is striking that, in the enforced absence of an N—H···π(arene) hydrogen bond of the type found in (II), the structure of (I) has nonetheless adjusted to maximize the effects of the weaker hydrogen bonds, in particular, by engaging both of the aryl rings in the molecule.

Within the molecule of (I), the C—C, C—N and N—O distances (Table 1) exhibit the usual pattern found (Quesada, Marchal *et al.*, 2002; Quesada, Low *et al.*, 2002) in 2,4-diamino-5-nitrosopyrimidines, consistent with extensive charge delocalization, as in (I*a*) (see *Scheme*). The conformation, as defined by the key torsion angles (Table 1), has atoms C27 and C67 effectively coplanar with the pyrimidine ring, but the phenyl rings are rotated out of this plane. The ester group has an unusual conformation (Fig. 1), as demonstrated by the (−)synclinal torsion angle C8—O82—C9—C10 (Table 1).

Experimental

A solution of ethyl glycinate hydrochloride (0.51 mmol) in ethanol (5 ml) was neutralized with KOH (0.51 mmol). 2-Benzylamino-4,6-bis(benzyloxy)-5-nitrosopyrimidine (0.47 mmol) was then added and the mixture was kept at 333 K for 6 h. When the mixture had cooled to room temperature, distilled water (50 ml) was added and ethanol was eliminated at reduced pressure until a solid precipitate appeared. The solid was then filtered off and washed with distilled water (yield 86%, m.p. 396 K). Analysis found: C 62.70, H 5.50, N 16.62%; $C_{22}H_{23}N_5O_4$ requires C 62.40, H 5.62, N 16.07%. Crystals suitable for single-crystal X-ray diffraction analysis were grown from a solution in ethanol–water (1:1, *v*/*v*).

Crystal data

$C_{22}H_{23}N_5O_4$	$D_x = 1.363$ Mg m^{-3}
$M_r = 421.45$	Mo *Kα* radiation
Monoclinic, $P2_1/c$	Cell parameters from 4644 reflections
$a = 15.2278$ (8) Å	$\theta = 3.0$–$25.0°$
$b = 15.8992$ (5) Å	$\mu = 0.10$ mm^{-1}
$c = 8.5558$ (3) Å	$T = 120$ (2) K
$\beta = 97.5860$ (11)°	Needle, purple
$V = 2053.31$ (14) Å^3	0.40 × 0.05 × 0.02 mm
$Z = 4$	

Data collection

Nonius KappaCCD diffractometer	$R_{\rm int} = 0.200$
φ scans, and ω scans with κ offsets	$\theta_{\rm max} = 25.0°$
24 714 measured reflections	$h = -18 \rightarrow 18$
3619 independent reflections	$k = -18 \rightarrow 18$
1861 reflections with $I > 2\sigma(I)$	$l = -10 \rightarrow 9$

Table 1
Selected geometric parameters (Å, °).

N1—C2	1.376 (5)	C2—N2	1.321 (5)
C2—N3	1.348 (5)	C4—N4	1.334 (5)
N3—C4	1.330 (5)	C5—N5	1.337 (5)
C4—C5	1.443 (5)	N5—O5	1.280 (4)
C5—C6	1.427 (6)	C6—O6	1.342 (5)
C6—N1	1.288 (5)		
N1—C2—N2—C27	175.8 (3)	C5—C6—O6—C67	−179.3 (3)
C2—N2—C27—C21	83.1 (5)	C6—O6—C67—C61	−77.5 (4)
N2—C27—C21—C22	−113.8 (4)	O6—C67—C61—C62	110.6 (4)
C5—C4—N4—C7	165.8 (3)	N4—C7—C8—O82	−178.2 (3)
C4—N4—C7—C8	−81.4 (5)	C7—C8—O82—C9	179.2 (3)
N4—C7—C8—O81	1.9 (6)	C8—O82—C9—C10	−76.9 (4)

Table 2
Hydrogen-bonding and short intermolecular contact geometry (Å, °).

*Cg*2 and *Cg*3 are the centroids of rings C21–C26 and C61–C66, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4—H4···O5	0.88	2.00	2.621 (4)	126
N2—H2···O5^{i}	0.88	2.06	2.933 (4)	175
N2—H2···N5^{i}	0.88	2.27	3.004 (5)	141
C62—H62···O5^{i}	0.95	2.50	3.369 (5)	152
C7—H7*B*···O81^{ii}	0.99	2.43	3.265 (5)	141
C22—H22···O81^{ii}	0.95	2.45	3.364 (4)	161
C7—H7*A*···*Cg*2^{ii}	0.99	2.47	3.439 (4)	165
C67—H67*A*···*Cg*3^{iii}	0.99	2.52	3.499 (4)	172

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

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Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.069$
$wR(F^2) = 0.176$
$S = 1.04$
3619 reflections
281 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0658P)^2 + 1.1859P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.28$ e Å^{-3}
$\Delta\rho_{\min} = -0.28$ e Å^{-3}

Compound (I) crystallized in the monoclinic system; space group $P2_1/c$ was uniquely assigned from the systematic absences. H atoms were treated as riding, with C—H distances in the range 0.95–0.99 Å and N—H distances of 0.88 Å.

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: *PLATON* (Spek, 2002); software used to prepare material for publication: *SHELXL*97 and *PRPKAPPA* (Ferguson, 1999).

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: NA1576). Services for accessing these data are described at the back of the journal.

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