Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

6-Amino-2-(3,4-dimethoxybenzylamino)-3-methyl-5-nitrosopyrimidin-4(3*H*)-one: hydrogen-bonded sheets form interdigitated bilayers

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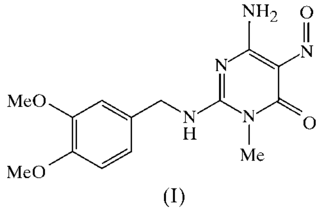
Received 14 March 2003
Accepted 17 March 2003
Online 10 April 2003

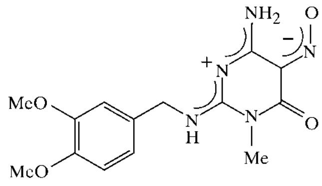
Molecules of the title compound, $C_{14}H_{17}N_5O_4$, exhibit a highly polarized molecular–electronic structure. The molecules are linked into sheets by two N—H···O hydrogen bonds [H···O = 2.03 and 2.02 Å, N···O = 2.836 (2) and 2.887 (2) Å, and N—H···O = 153 and 168°], augmented by a single C—H···O hydrogen bond [H···O = 2.47 Å, C···O = 3.403 (2) Å and C—H···O = 166°]. Pairs of sheets, related by inversion, form bilayers with interdigitated dimethoxybenzyl substituents, weakly linked by a further C—H···O interaction [H···O = 2.50 Å, C···O = 3.350 (2) Å and C—H···O = 146°].

Comment

The title compound, (I) (Fig. 1), has been prepared for use as an intermediate in the preparation of new heterocycles containing the pyrimidine nucleus. The bond distances in (I) (Table 1) show the pattern now familiar for compounds containing this type of substituted oxopyrimidine ring (Low *et al.*, 2000; Low, Moreno *et al.*, 2001; Low, Cannon *et al.*, 2001; Low, Arranz, Cobo, Fontecha, Godino, López & Glidewell, 2001; Low, Arranz, Cobo, Fontecha, Godino, López, Cannon *et al.*, 2001; Glidewell *et al.*, 2002; Low *et al.*, 2002). In particular, the sequence of four N—C bonds between atoms N2 and N4 all have similar lengths, so that it is not possible to describe the individual bonds in this sequence as being either single or double bonds; moreover, both of the exocyclic bonds in this sequence are much shorter than typical C(aryl)—NH_2 or C(aryl)—NH*R* distances (Allen *et al.*, 1987). On the other hand, the distances C5—N5 and N5—O5 differ by less than 0.05 Å, whereas in simple neutral compounds where there is no possibility of significant electronic delocalization, these distances normally differ by at least 0.20 Å (Talberg, 1977; Schlemper *et al.*, 1986) and the N—O distance rarely exceeds 1.25 Å (Davis *et al.*, 1965; Bauer & Andreassen, 1972; Talberg, 1977; Schlemper *et al.*, 1986). Finally, the C4—C5 and C5—C6 distances are very similar, with again no possibility of distinguishing here between single and double bonds. These observations, taken together, indicate the polarized form (I*a*) as the dominant contributor to the overall molecular–electronic structure, at the expense of the classically localized form (I).



(I)



(I*a*)

Within the dimethoxyphenyl fragment, the exocyclic C—C—O angles show the usual pattern observed for methoxyaryl compounds (Seip & Seip, 1973; Ferguson *et al.*, 1996; Patterson *et al.*, 1998), in which the C—C—O angles *cisoid* to the substituents are much larger than 120°, while those *transoid* are very much smaller. At the same time, the C—O—C angles are well in excess of tetrahedral values, consistent with the occurrence of repulsive interactions between the methyl groups and the neighbouring aryl C—H units.

The nitroso substituent is essentially coplanar with the pyrimidine ring, and the two methoxy groups are nearly coplanar with the aryl ring, while methylene atom C27 is also nearly coplanar with the pyrimidine ring; however, the torsion angles C2—N2—C27—C21 and N2—C27—C21—C22

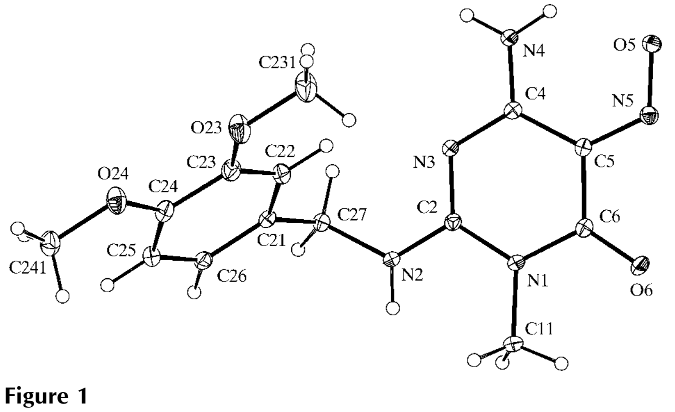


Figure 1
The molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

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DOI: 10.1107/S0108270103006231 © 2003 International Union of Crystallography

(Table 1) indicate that the two ring systems are very far from being coplanar. Thus, while the molecule as a whole could adopt a conformation having mirror symmetry, it does not do so, and this may be a consequence of direction-specific intermolecular forces, in particular the hydrogen bonds.

Within the molecule of (I) there is an N—H···O hydrogen bond (Table 2), with the nitroso O atom acting as acceptor in the formation of an *S*(6) motif (Bernstein *et al.*, 1995). The molecules are linked into sheets by two hard (Desiraju & Steiner, 1999) hydrogen bonds, both of the N—H···O type, augmented by a soft C—H···O hydrogen bond. Amino atom N4 in the molecule at (*x*, *y, z*) acts as hydrogen-bond donor, *via* H4*A*, to amide atom O6 in the molecule at (*x*, 1 + *y, z*), so generating by translation a *C*(6) chain running parallel to the [010] direction. In addition, amino atom N2 in the molecule at (*x*, *y*, *z*) acts as hydrogen-bond donor to nitroso atom O5 in the molecule at $(x, \frac{1}{2} - y, \frac{1}{2} + z)$, while N2 at $(x, \frac{1}{2} - y, \frac{1}{2} + z)$, in turn, acts as donor to O5 at (*x*, *y*, 1 + *z*), so producing a *C*(8) chain running parallel to the [001] direction and generated by the *c*-glide plane at $y = \frac{1}{4}$. The formation of this [001] chain is reinforced by a C—H···O hydrogen bond, in which atom C26 at (*x*, *y*, *z*) acts as donor to amide atom O6 at $(x, \frac{1}{2} - y, \frac{1}{2} + z)$. Hence, the [001] motif is better represented as a $C(8)C(9)[R_2^2(11)]$ chain of rings (Bernstein *et al.*, 1995). The combination of the [010] and [001] chains generates a sheet parallel to (100) containing *S*(6), $R_2^2(11)$ and $R_5^3(21)$ rings, in the latter of which there are double acceptors (Fig. 2).

In the formation of the reference (100) sheet, the network formed by the hard hydrogen bonds is almost planar, lying in the domain $0.35 < x < 0.39$, with the pendent dimethoxybenzyl substituents all lying on the same side of the sheet (Fig. 2). A second hydrogen-bonded network, related to the first by inversion, lies in the domain $-0.39 < x < -0.35$, with the dimethoxybenzyl substituents all lying on the same side of the sheet, in a sense opposite from those in the reference sheet. There is thus close interdigitation of the aryl substituents of these two sheets (Fig. 3), and a further C—H···O interaction (Table 2) may provide a weak link between the paired sheet. Atom C241 at (*x*, *y*, *z*) lies in a substituent pendent from the reference network in the domain $0.35 < x < 0.39$, and it acts as a hydrogen-bond donor to nitroso atom O5 in the molecule at $(-x, \frac{1}{2} + y, \frac{1}{2} - z)$, which forms part of the hydrogen-bonded network in the domain $-0.39 < x < -0.35$. Hence, pairs of (100) sheets form interdigitated and weakly linked bilayers, but with no direction-specific interactions between adjacent bilayers (Fig. 3). There are no aromatic π–π-stacking interactions either within or between adjacent sheets.

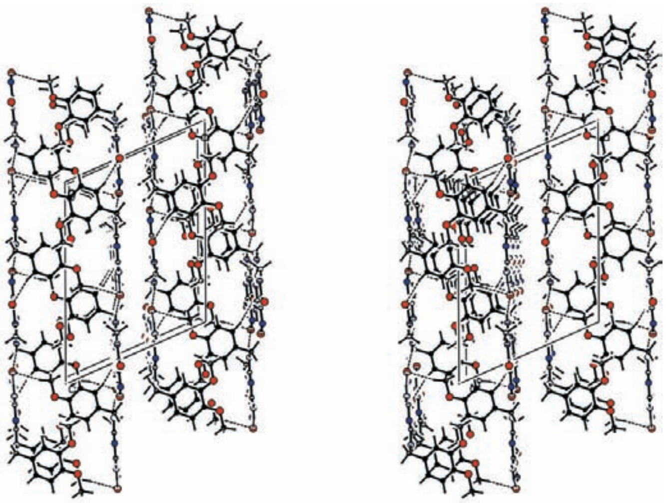

Figure 3
Stereoview of part of the crystal structure of (I), showing the formation of interdigitated (100) bilayers.

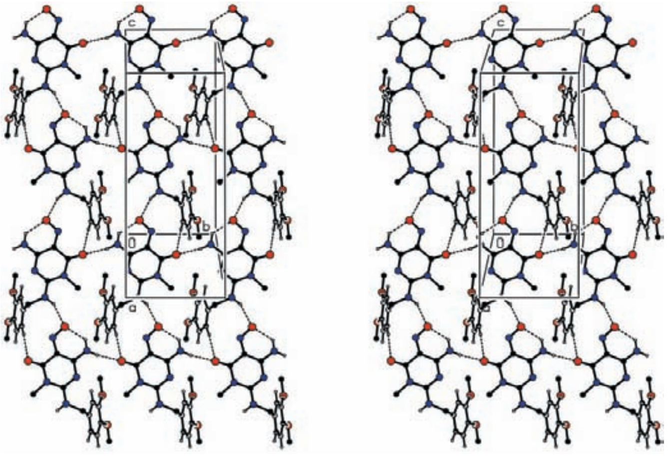

Figure 2
Stereoview of part of the crystal structure of (I), showing the formation of a (100) sheet. For the sake of clarity, methyl H atoms have been omitted.

It is of interest to note that while nitroso atom O5 acts as a threefold acceptor of hydrogen bonds (Table 2), consistent with its highly anionic nature, and amide atom O6 acts as a double acceptor, the two O atoms in the methoxy groups play no role whatsoever in the intermolecular aggregation.

Experimental

A suspension of 6-amino-2-methoxy-3-methyl-5-nitrosopyrimidin-4(3*H*)-one (0.10 g, 0.543 mmol), 3,4-dimethoxybenzylamine (0.364 g, 2.18 mmol) and methanol (4 ml) was stirred at room temperature for 30 min. The pink solid which formed was collected by filtration and washed with methanol (89% yield; m.p. 496 K). NMR: δ_H (300 MHz, DMSO-d_6) 3.36 (3H, *s*), 3.71 (3H, *s*), 3.73 (3H, *s*), 4.55 (2H, *s*), 6.87 (1H, *d*, *J* = 9.0 Hz), 6.91 (1H, *d*, *J* = 9.0 Hz), 7.02 (1H, *s*), 8.31 (1H, *d*, *J* = 4.5 Hz, NH), 8.49 (1H, *br s*, NH), 10.89 (1H, *d*, *J* = 4.5 Hz, NH); δ_C (75 MHz, DMSO-d_6) 27.4 (CH_2), 44.4 (CH_3—N), 55.5 and 55.6 (2 × CH_3—O), 111.6, 111.8, 119.8, 130.8, 142.1, 148.0, 148.6, 149.9, 154.5 and 161.6 (aromatic and heterocyclic). IR (cm^{-1}, KBr): 3335 (NH), 3200 (NH), 3180 (NH), 1681 (C═O), 1458 (N═O). MS (70 eV CI): *m*/*e* (%) 303 (92), 302 (87), 275 (32), 191 (21), 151 (100), 43 (40), 42 (41). It was also possible to obtain compound (I) in a comparable yield from 6-amino-3-methyl-5-nitroso-2-(methylhio)pyrimidin-4(3*H*)-one, under similar reaction conditions. Crystals suitable for single-crystal X-ray diffraction were grown from a solution in dimethyl sulfoxide.

Crystal data

$C_{14}H_{17}N_5O_4$
$M_r = 319.33$
Monoclinic, $P2_1/c$
$a = 12.8488$ (10) Å
$b = 7.4416$ (10) Å
$c = 16.962$ (2) Å
$\beta = 113.728$ (8)°
$V = 1484.7$ (3) Å^3
$Z = 4$

$D_x = 1.429$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3378 reflections
$\theta = 3.0$–27.4°
$\mu = 0.11$ mm^{-1}
$T = 120$ (2) K
Block, pink
0.60 × 0.30 × 0.20 mm

Data collection

Nonius KappaCCD diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*DENZO–SMN*; Otwinowski & Minor, 1997)
$T_{min} = 0.942$, $T_{max} = 0.979$
22 739 measured reflections

3378 independent reflections
2545 reflections with $I > 2\sigma(I)$
$R_{int} = 0.074$
$\theta_{max} = 27.4°$
$h = -16 \rightarrow 16$
$k = -9 \rightarrow 8$
$l = -21 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.117$
$S = 1.04$
3378 reflections
211 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0612P)^2 + 0.3970P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.29$ e Å^{-3}
$\Delta\rho_{min} = -0.30$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N1—C2	1.378 (2)	N1—C11	1.464 (2)
C2—N3	1.328 (2)	C2—N2	1.323 (2)
N3—C4	1.334 (2)	C4—N4	1.314 (2)
C4—C5	1.446 (2)	C5—N5	1.334 (2)
C5—C6	1.451 (2)	N5—O5	1.290 (2)
C6—N1	1.392 (2)	C6—O6	1.223 (2)
O23—C23—C22	125.47 (15)	O24—C24—C23	115.33 (14)
O23—C23—C24	114.61 (14)	O24—C24—C25	125.18 (15)
C23—O23—C231	116.67 (14)	C24—O24—C241	115.88 (13)
N1—C2—N2—C27	−178.2 (2)	C22—C23—O23—C231	0.1 (3)
C2—N2—C27—C21	−100.4 (2)	C25—C24—O24—C241	3.4 (2)
N2—C27—C21—C22	68.9 (2)	C4—C5—N5—O5	2.4 (2)

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2···O5^{i}	0.88	2.03	2.836 (2)	153
N4—H4A···O6^{ii}	0.88	2.02	2.887 (2)	168
N4—H4B···O5	0.88	1.96	2.616 (2)	130
C26—H26···O6^{i}	0.95	2.47	3.403 (2)	166
C241—H24A···O5^{iii}	0.98	2.50	3.350 (2)	146

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

The crystals of (I) are monoclinic and the space group $P2_1/c$ was uniquely assigned from the systematic absences. All H atoms were treated as riding, with C—H distances of 0.95 (aromatic), 0.98 (CH_3) or 0.99 Å (CH_2), 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, 2003); 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. RA and JQ thank COLCIENCIAS and Universidad del Valle for financial support. The authors thank their colleagues Justo Cobo and Adolfo Sánchez of the Universidad de Jaén for their support and great encouragement of this work.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1629). Services for accessing these data are described at the back of the journal.

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