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Hydrogen bonding in nitroaniline analogues: a hydrogen-bonded chain of rings in 2-amino-4-butylamino-6-methoxy-5-nitropyrimidine

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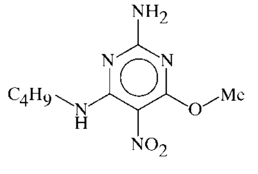
In the title compound, $C_9H_{15}N_5O_3$, in which the molecules exhibit orientational disorder, the molecules of the major component are linked by paired N—H···O hydrogen bonds [H···O = 2.37 and 2.39 Å, N···O = 2.974 (3) and 3.011 (3) Å, and N—H···O = 126 and 128°] to form a $C(8)C(8)[R^2_2(6)]$ chain of rings along [010]. The minor component (6.5% of the molecules) forms a similar chain running in the opposite direction.

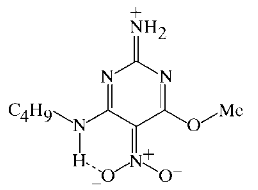
Comment

An important mode of supramolecular aggregation in 4-nitroanilines is based on the formation of N—H···O hydrogen bonds, with each molecule acting as both a double donor and a double acceptor in these bonds. The resulting supramolecular structures can be two- (Tonogaki *et al.*, 1993; Glidewell *et al.*, 2002) or three-dimensional (Ferguson *et al.*, 2001). An alternative aggregation mode can occur when there are bulky substituents present, which sometimes force an alternative one-dimensional aggregation mode in which the molecules are linked by paired N—H···O hydrogen bonds to form an $R^2_2(6)$ (Bernstein *et al.*, 1995) motif (McWilliam *et al.*, 2001; Glidewell *et al.*, 2002).

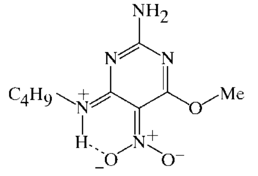
Continuing our study (Glidewell *et al.*, 2003) of 2-amino-5-nitropyrimidines, which are closely analogous to 4-nitroanilines but which also offer the possibility that intermolecular N—H···N hydrogen bonds might compete with N—H···O hydrogen bonds, we report here the molecular and supramolecular structure of 2-amino-4-butylamino-6-methoxy-5-nitropyrimidine, (I).



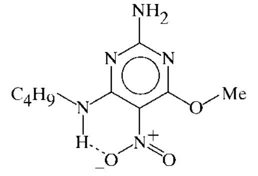
(I)



(I*a*)



(I*b*)



(I*c*)

The molecules of (I), which lie in general positions, exhibit orientational disorder. The two components, the site-occupancy factors of which are 0.935 and 0.065, are related by an apparent rotation of 180° approximately around the N4···O6 line (Fig. 1). Within the molecules of the major component, the bond lengths (Table 1) show clear evidence of extensive bond fixation, consequent upon the polarization of the molecular electronic structure. Thus, the exocyclic C2—N2 and C5—N5 bonds are both very short for their types; the mean literature values for bonds of these types are 1.355 and 1.468 Å, respectively (Allen *et al.*, 1987). The nitro group is essentially coplanar with the pyrimidine ring (Table 1), and the N—O distances are both longer than the mean literature value of 1.217 Å. It is noteworthy that the C2—N3 bond is shorter than C2—N1, and that N1—C6 is shorter than N3—C4, while N5—O52 is shorter than N5—O51. Taken together, these observations indicate that the polarized forms (I*a*), (I*b*) and (I*c*) are all significant contributors to the overall electronic structure.

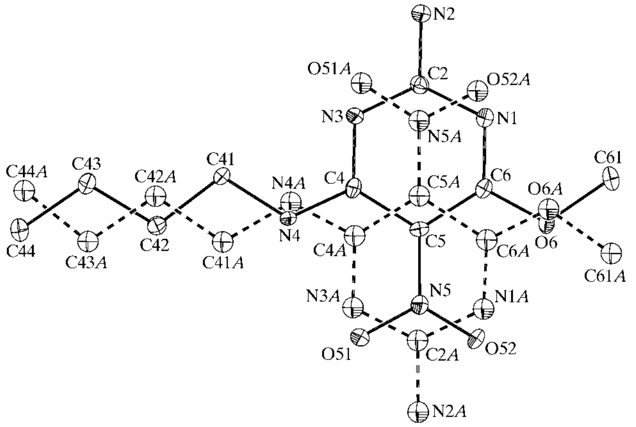


Figure 1
The molecular components of compound (I), showing the atom-labelling scheme and the relative orientation of the two components; full lines indicate the major component, broken lines the minor. For the sake of clarity, H atoms have been omitted. Displacement parameters are drawn at the 30% probability level. For the minor component, non-H atoms were assigned a common isotropic displacement parameter.

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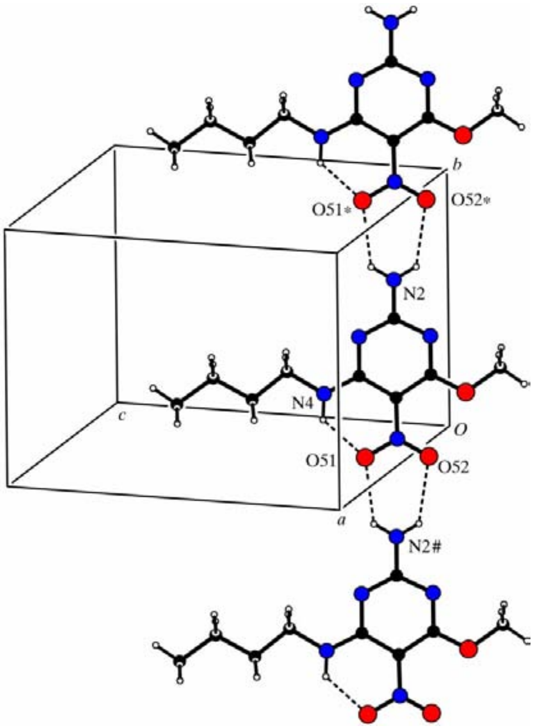

Figure 2
Part of the crystal structure of (I), showing the formation of a chain of rings along [010]. For the sake of clarity, only the major orientation is shown. Atoms marked with an asterisk (*) or hash sign (#) are at the symmetry positions (x, $1 + y$, z) and (x, $y - 1$, z), respectively.

The nature of the hydrogen bonding in (I) means that the supramolecular structures of the major and minor components are essentially the same, differing only in the direction of the chain formation (Table 2), and hence we discuss here only the major form. There is an intramolecular N—H···O hydrogen bond involving atoms N4 and O51 typical of those found in 2-nitroanilines (Dhaneshwar *et al.*, 1978; Ellena *et al.*, 1999; Cannon *et al.*, 2001), but the principal interest in (I) lies in the intermolecular hydrogen bonding. The amino atom N2 in the molecule at (x, y, z) acts as a hydrogen-bond donor, *via* atoms H11 and H22, respectively, to atoms O51 and O52 in the molecule at (x, $1 + y$, z), so generating a $C(8)C(8)[R_2^2(6)]$ chain of rings (Bernstein *et al.*, 1995) running parallel to the [010] direction (Fig. 2). The $R_2^2(6)$ ring is effectively planar, with the sum of the internal angles being 718°. It is notable that the supramolecular aggregation in (I) involves only N—H···O hydrogen bonds, whereas in analogous 2-amino-4,6-dimethoxy-5-nitropyrimidine (Glidewell *et al.*, 2003), both N—H···O and N—H···N hydrogen bonds contribute to the supramolecular structure.

Eight chains of rings pass through each unit cell of (I), but there are neither hydrogen bonds nor aromatic π–π-stacking interactions between adjacent chains, so that the supramolecular structure defined by the direction-specific interactions is just one-dimensional. The total number of hydrogen bonds within the structure is maximized if the orientation of the molecules is fully correlated within a given chain. There is no necessary correlation between the molecular orientations in different chains, and chains containing the minor orientation are thus likely to be randomly distributed throughout the structure.

In the previously observed examples of such a chain of rings, the chains in the triclinic polymorph of 2-iodo-4-nitroaniline are linked into sheets by means of a two-centre iodo–nitro interaction (McWilliam *et al.*, 2001), and in 2-trifluoromethyl-4-nitroaniline, a single C—H···O hydrogen bond links the molecules into a ladder generated by a 2_1 screw axis (Glidewell *et al.*, 2002). It seems probable that direction-specific interactions between the chains in (I) are prevented by the presence of the *N*-butyl substituent which, in both components, adopts the usual all-*trans* chain-extended conformation (Table 1).

Experimental

A sample of 2-amino-4-butylamino-6-methoxy-5-nitrosopyrimidine (Marchal, 2001) was converted into (I) by oxidation using 3-chloroperoxobenzoic acid (1.1 molar equivalents) in acetonitrile solution. After recrystallization from ethyl acetate, (I) had a melting point of 378 K. Spectroscopic analysis, ^{1}H NMR (δ, DMSO-d_6): 0.90 (t, 3H, C–CH$_3$, J = 7.41 Hz), 1.32 (m, 2H, CH$_2$), 1.55 (m, 2H, CH$_2$), 3.45 (m, 2H, CH$_2$), 3.88 (s, 3H, O–CH$_3$), 7.37 (bs, 2H, NH$_2$, exchanges with H$_2$O), 8.84 (t, 1H, NH, J = 5.49 Hz); ^{13}C NMR (δ, DMSO-d_6): 13.6, 19.5, 30.7, 54.2, 109.2, 157.9, 160.6, 165.3. Crystals of (I) suitable for single-crystal X-ray diffraction were grown by slow evaporation of a solution in water–ethanol–acetonitrile (1:1:1 v/v).

Crystal data

$C_9H_{15}N_5O_3$
$M_r = 241.26$
Monoclinic, $C2/c$
$a = 20.5825$ (13) Å
$b = 8.8102$ (4) Å
$c = 13.0289$ (11) Å
$\beta = 109.810$ (3)°
$V = 2222.8$ (3) Å^3
$Z = 8$

$D_x = 1.442$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2482 reflections
$\theta = 3.2$–27.4°
$\mu = 0.11$ mm^{-1}
$T = 120$ (1) K
Plate, colourless
0.22 × 0.08 × 0.02 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*DENZO–SMN*; Otwinowski & Minor, 1997)
$T_{\min} = 0.911$, $T_{\max} = 0.998$
16 040 measured reflections

2482 independent reflections
1151 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.124$
$\theta_{\max} = 27.4°$
$h = -26 \rightarrow 26$
$k = -10 \rightarrow 11$
$l = -16 \rightarrow 16$

Table 1
Selected geometric parameters (Å, °).

N1—C2	1.361 (4)	C2—N2	1.327 (4)
C2—N3	1.335 (4)	C4—N4	1.335 (4)
N3—C4	1.342 (4)	C5—N5	1.407 (4)
C4—C5	1.446 (4)	N5—O51	1.265 (3)
C5—C6	1.418 (4)	N5—O52	1.227 (3)
C6—N1	1.316 (4)	C6—O6	1.330 (4)

N4—C41—C42—C43	176.9 (3)
C41—C42—C43—C44	−179.7 (3)
C4—C5—N5—O51	−0.5 (4)
C4—C5—N5—O52	178.5 (3)
N4*A*—C41*A*—C42*A*—C43*A*	173 (5)
C41*A*—C42*A*—C43*A*—C44*A*	−175 (4)
C4*A*—C5*A*—N5*A*—O51*A*	6 (8)
C4*A*—C5*A*—N5*A*—O52*A*	−177 (5)

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Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.063$
$wR(F^2) = 0.163$
$S = 0.94$
2482 reflections
211 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0759P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.32$ e Å^{-3}
$\Delta\rho_{\min} = -0.31$ e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N4—H4···O51	0.88	1.93	2.583 (3)	130
N2—H21···O51$^{\rm i}$	0.88	2.37	2.974 (3)	126
N2—H22···O52$^{\rm i}$	0.88	2.39	3.011 (3)	128
N4*A*—H4*A*···O51*A*	0.88	1.90	2.56 (4)	133
N2*A*—H21*A*···O51*A*$^{\rm ii}$	0.88	2.31	3.00 (4)	132
N2*A*—H22*A*···O52*A*$^{\rm ii}$	0.88	2.43	3.02 (4)	123

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

The systematic absences permitted *Cc* and *C*2/*c* as possible space groups; *C*2/*c* was selected and confirmed by the successful structure analysis. It was apparent at an early stage that the structure contained a small proportion of molecules adopting an alternative orientation. The bond distances in the minor component were constrained using *DFIX* commands (*SHELXL*97; Sheldrick, 1997), and the non-H atoms were assigned a common isotropic displacement parameter. Refinement of the site-occupancy factors for the two components, constrained to sum to unity, gave values of 0.912 (4) and 0.088 (4) for the major and minor components, respectively. However, in these circumstances, the common $U_{\rm iso}$ value for the minor component was more than double the mean of the $U_{\rm eq}$ values for the major component. Refinements were then carried out with a series of fixed values for the site-occupancy factors, which were still constrained to sum to unity. The most satisfactory outcome, in terms of the values of $U_{\rm iso}$ and the mean $U_{\rm eq}$ for the two components, was achieved when the occupancies were 0.935 and 0.065, and accordingly the occupancies were thereafter fixed at these values. H atoms were treated as riding, with C—H distances of 0.98 (CH_3) and 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; molecular graphics: *PLATON* (Spek, 2002); software used to prepare material for publication: *SHELXL*97 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: SK1600). Services for accessing these data are described at the back of the journal.

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