

2-Amino-5-nitro-4,6-dipiperidino-pyrimidinium hydrogensulfate mono-hydrate: hydrogen-bonded sheets containing highly distorted cations

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Received 14 January 2003

Accepted 16 January 2003

Online 11 February 2003

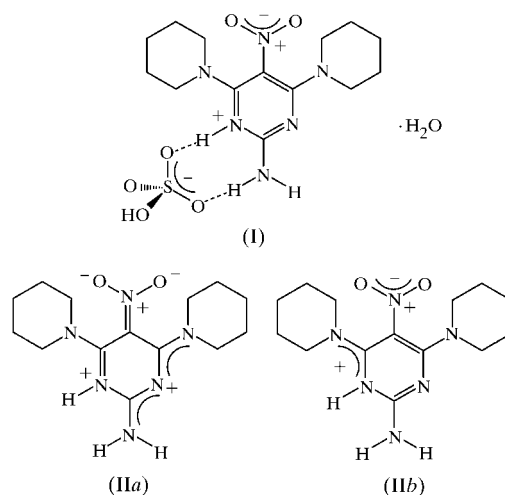
In the title compound, $C_{14}H_{23}N_6O_2^+ \cdot HSO_4^- \cdot H_2O$, the pyrimidinium ring of the cation adopts a twist-boat conformation, induced by steric clashes between adjacent ring substituents; the anions and the water molecules are linked by three $O \cdots H \cdots O$ hydrogen bonds [$H \cdots O = 1.70\text{--}1.78 \text{ \AA}$, $O \cdots O = 2.548(2)\text{--}2.761(2) \text{ \AA}$ and $O-H \cdots O = 161\text{--}168^\circ$] into chains of edge-fused $R_4^4(12)$ rings, which are linked into sheets by the cations, *via* three $N-H \cdots O$ hydrogen bonds [$H \cdots O = 1.96\text{--}2.17 \text{ \AA}$, $N \cdots O = 2.820(2)\text{--}2.935(2) \text{ \AA}$ and $N-H \cdots O = 145\text{--}173^\circ$].

Comment

We have recently described the structure of 2-amino-4,6-bis(1-pyrrolidyl)-5-nitrosopyrimidine (Quesada *et al.*, 2002). In this compound, the pyrimidine ring is considerably distorted from planarity, and this was interpreted as resulting from the compromise between maximizing the electronic delocalization between the amino substituents and the nitroso group, and the relief of steric hindrance between adjacent substituents, in particular, the nitroso group lying between the two pyrrolidyl substituents. The question then arises concerning the behaviour of an analogous system containing a nitro substituent at the 5-position, which is not only bulkier than a nitroso substituent, but may be expected to be a stronger electron acceptor. Accordingly, we have synthesized several 2-amino-5-nitropyrimidines containing secondary amino substituents (*viz.* 1-pyrrolidinyl, 1-piperidyl and 4-morpholinyl) at positions 4 and 6. Of these, only the piperidyl derivative has so far been crystallized, as a hydrated hydrogensulfate salt, (I), in

which a single H atom has been transferred from the acid component to one of the ring N atoms of the pyrimidine.

The pyrimidinium cation in (I) exhibits an unusual pattern of bond lengths (Table 1). Firstly, the exocyclic C—N bonds are all short for their types; the mean values (Allen *et al.*, 1987) for $C_{ar}\text{—}NH_2$, $C_{ar}\text{—}NR_2$ and $C_{ar}\text{—}NO_2$ bond lengths (*ar* is aryl) are 1.355, 1.371 and 1.468 Å, respectively. Secondly, the pyrimidine-ring N1—C2 and N1—C6 bond lengths are both much shorter than the C2—N3 bond. Finally, the nitro group N—O distances are both significantly longer than the mean value, 1.217 Å, for bonds of this type. These observations, taken together with the planarity at the piperidino N atoms, N4 and N6, are indicative of significant contributions to the overall electronic structure of polarized forms such as (IIa) and (IIb) (see *Scheme* below).



The participation of the piperidino N atoms in the electronic delocalization is surprising, in view of the likely steric clashing between the piperidine rings at positions 4 and 6 and the nitro group at position 5; avoidance of such clashing *via* rotation of each of these adjacent substituents about their exocyclic C—N bonds might have been expected, although at the cost of the electron delocalization. Instead, this delocalization is maintained, but at the cost of a significant distortion of the pyrimidinium ring into a twist-boat conformation, with ring-puckering parameters (Cremer & Pople, 1975) $\theta = 105.9(5)^\circ$ and $\varphi = 82.9(5)^\circ$. This distortion may perhaps more readily be demonstrated by the torsion angles (Table 1), where for a fully planar system, those torsion angles within the pyrimidine ring would all be effectively 0° , while those involving one exocyclic atom would all be close to 180° . If we define a reference plane containing atoms C2, C4 and C6, the deviations of the N atoms from this plane are as follows: ring atoms N1 and N3, $-0.015(2)$ and $0.146(2) \text{ \AA}$, respectively; exocyclic N atoms N2, N4, N5 and N6, $-0.057(3)$, $0.111(3)$, $-1.273(3)$ and $0.257(3) \text{ \AA}$, respectively. Of the exocyclic N atoms, the largest deviations from the C2/C4/C6 plane are observed for the adjacent atoms N4, N5 and N6, with nitro atom N5 exhibiting the largest displacement, and on the side of the plane opposite from the displacements of atoms N4 and N6.

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This electronic interpretation receives strong support from a comparison of the structures of two related benzene derivatives. In 1-amino-2,4,6-trinitro-3,5-bis(1-piperidino)benzene [Cambridge Structural Database (CSD; Allen, 2002) refcode TEWJAG; Wolff *et al.*, 1996], where both electron-donor amino groups and electron-acceptor nitro groups are present, the benzene ring has a chair conformation. However, in 1,3,5-triisopropyl-2-nitrobenzene (CSD refcode HALJUZ; De Ridder *et al.*, 1993; Marsh, 1997), where there are no obvious

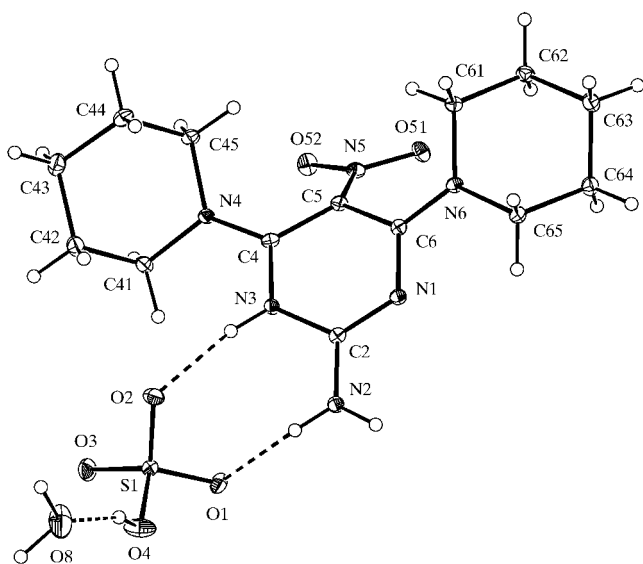


Figure 1
View of the independent components of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

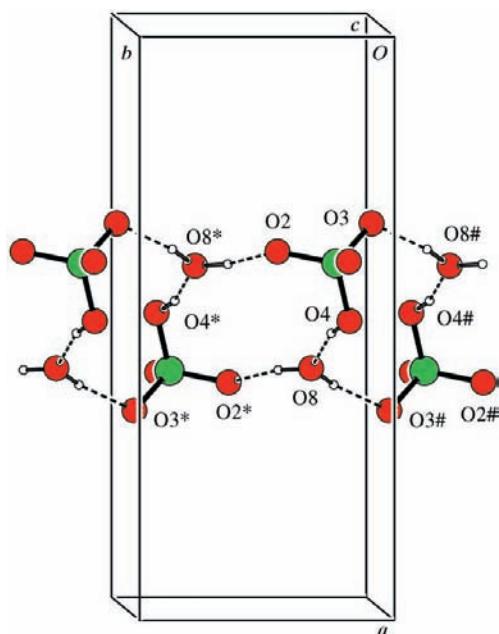


Figure 2
Part of the crystal structure of (I), showing the formation of a chain of edge-fused $R_4^1(12)$ rings running parallel to $[010]$ and comprising anions and water molecules only. Atoms marked with an asterisk (*) or hash (#) are at the symmetry positions $(1-x, 1-y, 1-z)$ and $(1-x, -y, 1-z)$, respectively.

electron-donor substituents, the benzene ring remains planar, while the nitro group is twisted into an almost orthogonal conformation.

Within the selected asymmetric unit (Fig. 1), atoms N2 and N3 act as hydrogen-bond donors to O1 and O2, respectively, while O4 acts as a hydrogen-bond donor to water atom O8. Three further hydrogen bonds, two of the O—H...O type and one of the N—H...O type (Table 2), link the three molecular components into continuous sheets, whose construction is most readily analysed in terms of the two-component one-dimensional substructure formed by the anions and the water molecules.

Water atom O8 at (x, y, z) acts as hydrogen-bond donor, *via* H81 and H82, respectively, to O3 in the anion at $(1-x, -y, 1-z)$ and to O2 in the anion at $(1-x, 1-y, 1-z)$; propagation by inversion of these two hydrogen bonds then generates a chain of edge-fused $R_4^1(12)$ (Bernstein *et al.*, 1995) rings, with rings containing O2 atoms centred at $(\frac{1}{2}, n+\frac{1}{2}, \frac{1}{2})$ ($n = \text{zero or integer}$) and rings containing O3 atoms centred at $(\frac{1}{2}, n, \frac{1}{2})$ ($n = \text{zero or integer}$) (Fig. 2). This chain of rings runs along the line $(\frac{1}{2}, y, \frac{1}{2})$ and a second such chain, related to the first by the action of the 2_1 screw axes, runs along the line $(\frac{1}{2}, y, 0)$. Adjacent chains are linked by the cations into (100) sheets.

The cation at (x, y, z) acts as donor, *via* H2B, to atom O1 in the anion at (x, y, z) , which forms part of the anion/water chain along $(\frac{1}{2}, y, \frac{1}{2})$; the same cation also acts as donor, *via* H2A, to O1 in the anion at $(1-x, \frac{1}{2}+y, \frac{1}{2}-z)$, which lies in the chain along $(\frac{1}{2}, y, 0)$. The amino group in the cation at $(1-x, 1-y,$

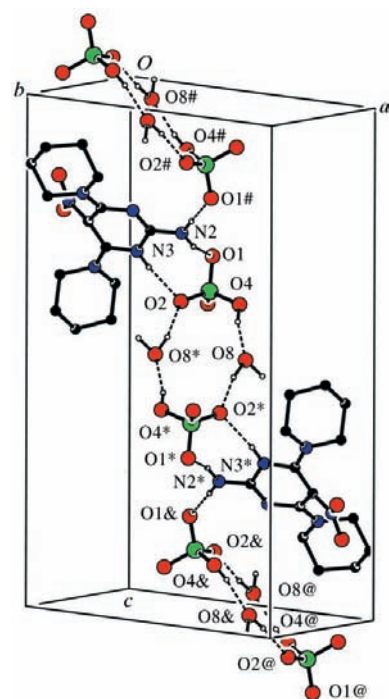


Figure 3
Part of the crystal structure of (I), showing the formation of a $[01\bar{1}]$ chain linking the $[010]$ anion/water chains into a (100) sheet. For the sake of clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*), hash (#), ampersand (&) or at sign (@) are at the symmetry positions $(1-x, 1-y, 1-z)$, $(1-x, \frac{1}{2}+y, \frac{1}{2}-z)$, $(x, \frac{1}{2}-y, \frac{1}{2}+z)$ and $(1-x, -\frac{1}{2}+y, \frac{3}{2}-z)$, respectively.

$1 - z$) likewise acts as donor to O1 atoms at $(1 - x, 1 - y, 1 - z)$ and $(x, \frac{1}{2} - y, \frac{1}{2} + z)$, which lie in the chains along $(\frac{1}{2}, y, \frac{1}{2})$ and $(\frac{1}{2}, y, 1)$. These interactions thus link the anion/water chain along $(\frac{1}{2}, y, \frac{1}{2})$ to those along $(\frac{1}{2}, y, 0)$ and $(\frac{1}{2}, y, 1)$, respectively (Fig. 3), and propagation of these links by inversion thus generates a (100) sheet centred at $x = \frac{1}{2}$. There are no direction-specific interactions between adjacent sheets. Despite the polarized nature of the cationic donor and the anionic acceptor, none of the N—H...O hydrogen bonds is particularly short (Table 2). The shortest of the O—H...O hydrogen bonds involves two essentially neutral O atoms.

Experimental

2-Amino-5-nitroso-4,6-dipiperidinopyrimidine (Marchal, 2001) was converted into 2-amino-5-nitroso-4,6-dipiperidinopyrimidine by oxidation with 1.1 molar equivalents of 3-chloroperoxybenzoic acid in acetonitrile solution. After work-up, including exposure of a solution of 2-amino-5-nitroso-4,6-dipiperidinopyrimidine to anhydrous sodium sulfate, used as a drying agent, the nitro compound crystallized as the hydrogensulfate salt. Crystals of (I) suitable for single-crystal X-ray diffraction were obtained by slow evaporation of a solution in water–ethanol–acetonitrile (1:1:1 by volume).

Crystal data

$C_{14}H_{23}N_6O_2^+ \cdot HSO_4^- \cdot H_2O$
 $M_r = 422.48$
 Monoclinic, $P2_1/c$
 $a = 14.0307$ (3) Å
 $b = 6.1277$ (1) Å
 $c = 21.5135$ (5) Å
 $\beta = 91.485$ (1)°
 $V = 1849.02$ (7) Å³
 $Z = 4$

$D_x = 1.518$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 4111 reflections
 $\theta = 3.4$ – 27.5 °
 $\mu = 0.23$ mm⁻¹
 $T = 120$ (2) K
 Needle, colourless
 $0.20 \times 0.04 \times 0.02$ mm

Data collection

Nonius KappaCCD diffractometer
 φ scans, and ω scans with κ offsets
 Absorption correction: multi-scan
 (DENZO-SMN; Otwinowski & Minor, 1997)
 $T_{\min} = 0.946$, $T_{\max} = 0.996$
 14 285 measured reflections

4111 independent reflections
 3452 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.057$
 $\theta_{\text{max}} = 27.5$ °
 $h = -13 \rightarrow 13$
 $k = -7 \rightarrow 7$
 $l = -27 \rightarrow 27$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.045$
 $wR(F^2) = 0.123$
 $S = 1.06$
 4111 reflections
 253 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0664P)^2 + 0.8404P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.58$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.65$ e Å⁻³

Space group $P2_1/c$ was uniquely assigned from the systematic absences. H atoms bonded to O atoms were located from difference maps and treated as riding atoms, with O—H distances derived from difference maps, viz. 0.82 (anion) and 0.99 Å (water). Other H atoms were treated as riding, with N—H distances of 0.88 Å and C—H distances of 0.99 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: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2002); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

Table 1

Selected geometric parameters (Å, °).

N1—C2	1.312 (2)	C2—N2	1.318 (2)
C2—N3	1.380 (2)	C4—N4	1.321 (2)
N3—C4	1.365 (2)	C5—N5	1.425 (2)
C4—C5	1.426 (2)	N5—O51	1.252 (2)
C5—C6	1.454 (2)	N5—O52	1.238 (2)
C6—N1	1.349 (2)	C6—N6	1.323 (2)
C4—N4—C41	124.08 (15)	C6—N6—C61	123.67 (15)
C4—N4—C45	122.44 (14)	C6—N6—C65	121.16 (14)
C41—N4—C45	113.48 (14)	C61—N6—C65	114.13 (13)
N1—C2—N3—C4	14.0 (2)	C2—N3—C4—N4	178.06 (15)
C2—N3—C4—C5	-1.4 (2)	C6—C5—C4—N4	163.43 (16)
N3—C4—C5—C6	-17.2 (2)	N3—C4—C5—N5	136.80 (16)
C4—C5—C6—N1	25.6 (2)	N1—C6—C5—N5	-127.89 (16)
C5—C6—N1—C2	-14.1 (2)	C2—N1—C6—N6	166.58 (15)
C6—N1—C2—N3	-5.7 (2)	C4—C5—C6—N6	-155.08 (16)

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N2—H2A...O1 ⁱ	0.88	2.02	2.896 (2)	173
N2—H2B...O1	0.88	2.17	2.935 (2)	145
N3—H3...O2	0.88	1.96	2.820 (2)	164
O4—H4...O8	0.82	1.75	2.548 (2)	163
O8—H81...O3 ⁱⁱ	0.99	1.70	2.656 (2)	161
O8—H82...O2 ⁱⁱⁱ	0.99	1.78	2.761 (2)	168

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

X-ray data were collected at the EPSRC X-ray Crystallographic Service, University of Southampton, England. JNL thanks NCR Self-Service, Dundee, for grants which have provided computing facilities for this work. We thank Dr M. Melguizo for his interest and advice.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1612). Services for accessing these data are described at the back of the journal.

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