metal-organic papers

2,4-Diamino-5-(3,4,5-trimethoxybenzyl)-pyrimidinium 4-hydroxy-3-nitrophenyl-arsonate monohydrate

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The crystal structure of the title compound, $(C_{14}H_{19}N_4O_3)$-$[AsO_2(OH)(C_6H_4NO_3)]\cdot H_2O$, consists of substituted pyrimidine cations, roxarsone (3-nitro-4-hydroxyphenylarsonate) anions and water molecules. Due to deprotonation of the arsonate group, the As—O bond distances in the anion are significantly different. An extensive network of O—H$\cdots$O, N—H$\cdots$O and N—H$\cdots$N hydrogen bonds helps to stabilize the crystal structure.

Comment

3-Nitro-4-hydroxyphenylarsonic acid (common name roxarsone) is an arsenic-containing compound that has anticoccidial action and promotes growth in animals. As part of our studies into its bioactivity, we have prepared the title roxarsonate-containing molecular salt, (I), and its crystal structure is presented here.

(I)
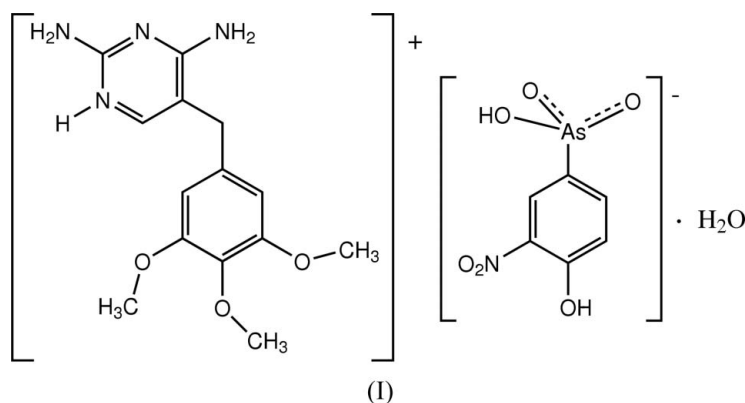
The crystal structure of (I) consists of substituted pyrimidinium cations, roxarsonate anions and water molecules of crystallization (Fig. 1). Within the roxarsone monoanion, the As—O2 bond distance is almost identical to that of As—O3, but significantly shorter than the As—O1 bond distance (Table 1), due to deprotonation of the arsonate group. The O atoms of the nitro group are disordered over two sites. Both conformations are tilted with respect to the C1-containing benzene ring plane, with dihedral angles of 27 (1) and 35 (2)° for the O5a- and O5b-nitro groups, respectively.

Within the substituted pyrimidine cation, the C12–C17 benzene ring is roughly perpendicular to the pyrimidine ring, the dihedral angle being 79.74 (11)°. The C atoms of the C18- and C19-methyl groups are coplanar with the benzene plane, their atomic deviations being 0.040 (8) and 0.054 (10) Å, respectively. Conversely, the C20-methyl C atom is out of the benzene plane by 1.248 (7) Å, thus minimizing the steric repulsion between adjacent –CH₃ groups.

An extensive network of O—H···O, N—H···O and N—H···N hydrogen bonds (Table 2) helps to stabilize the crystal structure of (I).

Experimental

2,4-Diamino-5-(3,4,5-trimethoxybenzyl)pyrimidine (5 mmol) and 3-nitro-4-hydroxyphenylarsonic acid (5 mmol) were dissolved in a water–ethanol mixture (50 ml, 4:1). The solution was stirred for 2 h at 323 K and then filtered. Single crystals of (I) were obtained from the filtrate after 3 weeks.

Crystal data

$(C_{14}H_{19}N_4O_3)[AsO_2(OH)$- $(C_6H_4NO_3)]\cdot H_2O$	$Z = 8$
$M_r = 571.38$	$D_x = 1.565$ Mg m^{-3}
Orthorhombic, $Pbca$	Mo $K\alpha$ radiation
$a = 8.1865$ (13) Å	$\mu = 1.47$ mm^{-1}
$b = 20.9285$ (16) Å	$T = 294$ (2) K
$c = 28.304$ (2) Å	Prism, yellow
$V = 4849.3$ (9) Å^3	$0.34 \times 0.30 \times 0.25$ mm

Data collection

Bruker APEXII diffractometer	24891 measured reflections
φ and ω scans	4489 independent reflections
Absorption correction: multi-scan	3922 reflections with $I > 2\sigma(I)$
$SADABS$ (Sheldrick, 2002)	$R_{int} = 0.046$
$T_{min} = 0.622$, $T_{max} = 0.700$	$\theta_{max} = 25.5°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0447P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.057$	$+ 5.6729P]$
$wR(F^2) = 0.119$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.21$	$(\Delta/\sigma)_{max} = 0.001$
4489 reflections	$\Delta\rho_{max} = 0.64$ e Å^{-3}
347 parameters	$\Delta\rho_{min} = -0.51$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected bond lengths (Å).

As—O1	1.720 (3)	As—O3	1.652 (3)
As—O2	1.664 (3)	As—C1	1.903 (3)

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2A···O3^i	0.95	1.87	2.817 (4)	176
N2—H2B···N4^i	0.96	2.48	3.318 (5)	146
N3—H3A···O7^{ii}	0.92	2.51	3.223 (4)	135
N3—H3B···O4^{iii}	0.92	2.33	3.139 (5)	147
N3—H3B···O5A^{iii}	0.92	2.48	3.078 (10)	123
N5—H5A···O3^i	0.94	1.70	2.607 (5)	162
O1—H1···O2^{iv}	0.93	1.67	2.582 (4)	165
O4—H4A···O1W	0.92	1.65	2.545 (4)	165
O1W—H1A···O2^v	0.86	1.83	2.687 (4)	171
O1W—H1B···O8^{vi}	0.89	2.46	3.221 (4)	143
O1W—H1B···O9^{vi}	0.89	2.01	2.767 (4)	142

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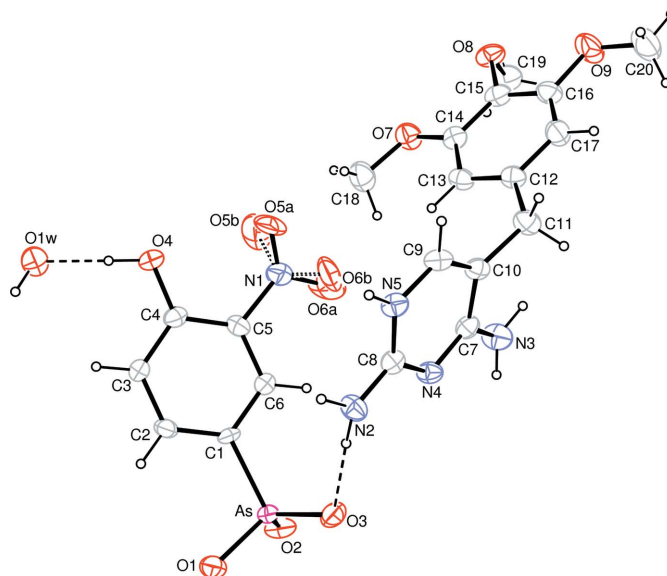

Figure 1
The molecular structure of (I) with 30% probability displacement ellipsoids (arbitrary spheres for H atoms). Dashed lines indicate hydrogen bonds. Suffixes a and b indicate the two disordered components of the nitro group.

The nitro group is disordered over two sites; the occupancies of the O atoms were refined and converged to 0.60 (3) for O5a/O6a and 0.40 (3) for O5b/O6b (occupancy sum constrained to unity). H atoms bonded to N and O atoms were located in a difference Fourier map and refined as riding in their as-found relative positions, with $U_{iso}(H) = 1.5U_{eq}(O,N)$ [N—H = 0.92–0.96 Å and O—H = 0.92–0.93 Å]. Methyl H atoms were placed in calculated positions, with C—H = 0.96 Å, and their torsion angles were refined to fit the electron density, with $U_{iso}(H) = 1.5U_{eq}(C)$. Other H atoms were placed in calculated positions, C—H = 0.93 Å (aromatic) or 0.97 Å (methylene), and refined in riding mode, with $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *SMART* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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