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Key indicators

Single-crystal X-ray study

 $T = 120$ KMean $\sigma(\text{C}-\text{C}) = 0.003$ Å R factor = 0.050 wR factor = 0.145

Data-to-parameter ratio = 15.1

 For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Bis(1,2,3,5-tetramethyl-4-nitropyrazolium) dihydronium tris(4-methyl-3,5-dinitrobenzenesulfonate) forms C(8) chains through O—H···O bonding *via* the dihydronium cation

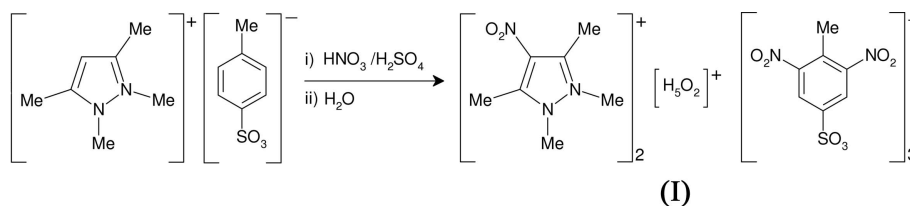
In the title salt, $2\text{C}_7\text{H}_{12}\text{N}_3\text{O}_2^+ \cdot \text{H}_5\text{O}_2^+ \cdot 3\text{C}_7\text{H}_5\text{N}_2\text{O}_7\text{S}^-$, strong hydrogen bonding from the donor (H_5O_2^+) group links to 4-methyl-3,5-dinitrobenzenesulfonate anions. The dihydronium (H_5O_2^+) cation could be considered intermediate between clearly distinct (H_3O^+) and H_2O entities and an ' $(\text{H}_5\text{O}_2)^+$ ' entity, although it tends to be closer to the former; the O···O distance is 2.434 (3) Å. Strong hydrogen bonding leads to the formation of chains along the [010] direction.

Received 20 February 2006

Accepted 8 March 2006

Comment

Reaction of 1,2,3,5-tetramethylpyrazolium 4-toluenesulfonate with fuming nitric acid and concentrated sulfuric acid leads to nitration of both the cation and the anion. The salt isolated after quenching in ice and recrystallization from ethanol was found to be the title salt, (I).



Two previous reports give support to this nitration reaction. A kinetic study has indicated that the cation of 1,2,3,5-tetramethylpyrazolium bisulfate undergoes nitration to give the 1,2,3,5-tetramethyl-4-nitropyrazolium cation in a mixture of fuming nitric acid and concentrated sulfuric acid (Burton *et al.*, 1971). In another study, 4-toluenesulfonyl chloride was reported to undergo nitration to give 4-methyl-3,5-dinitrobenzenesulfonic acid in a similar medium (Schmidt *et al.*, 1999).

The existence of the dihydronium (H_5O_2^+) unit was confirmed by the refinement. Initially, two O atoms (O1 and O2) were treated as water molecules and the associated H atoms were allowed to refine freely. On consideration of charge balance and the hydrogen-bonding scheme, and on examination of difference maps (visually using *PLATON*; Spek, 2003), it was believed likely that an additional H atom was located between the two water molecules [see, for example, Wells (1984) and Bernal & Fowler (1933)] but slightly closer to O2. Thus, an H atom was placed in this position and also refined freely, resulting in a position that was closer to O2, at a distance of 1.01 (5) Å. The group could be considered intermediate between clearly distinct (H_3O^+) and (H_2O) entities and an ' $(\text{H}_5\text{O}_2)^+$ ' entity, although it tends to be closer to the former. The O1···O2 distance is 2.434 (3) Å, with

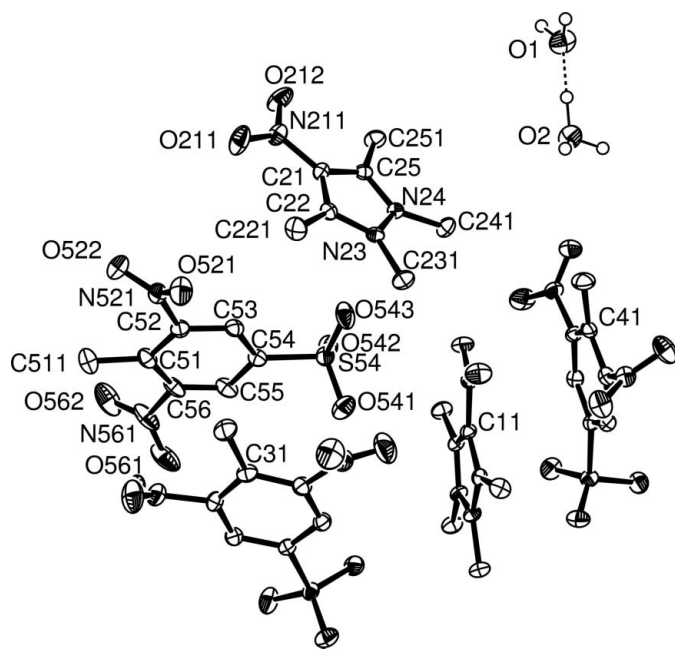


Figure 1

The asymmetric unit of the title compound, showing part of the atom-labelling scheme and indicating how it continues for similar ions within the asymmetric unit. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity, except those in the $(\text{H}_5\text{O}_2)^+$ unit, which are shown as circles of arbitrary radii.

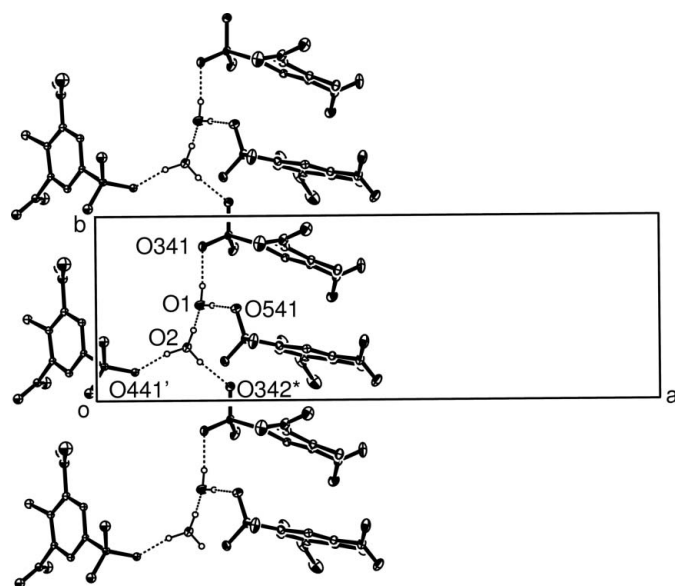


Figure 2

Part of the crystal structure of the title compound, showing the formation of hydrogen-bonded $C(8)$ chains along $[010]$. Atoms marked with an asterisk (*) or a prime (') are at the symmetry positions $(-x, 1-y, -z)$ and $(x, y-1, z)$, respectively. The two 1,2,3,5-tetramethyl-4-nitropyrazolium cations have been omitted for clarity, as have all H atoms, except those of the $(\text{H}_5\text{O}_2)^+$ unit, which are shown as circles of arbitrary radii. Displacement ellipsoids are drawn at the 30% probability level.

an $\text{O}-\text{H}\cdots\text{O}$ angle of $174(5)^\circ$; this distance is significantly shorter than for other $\text{O}-\text{H}\cdots\text{O}$ bonds within the structure (Table 1), again supporting the above interpretation.

Strong hydrogen bonds (Table 1) from the $\text{H}_2\text{O}\cdots\text{H}_3\text{O}^+$ unit link to sulfonate O atoms. Atom O1 hydrogen bonds within the asymmetric unit, whereas O2 not only hydrogen bonds to O1, but also to symmetry-related ions. This gives rise to $C(8)$ chains (Bernstein *et al.*, 1995) along the $[010]$ direction (Fig. 2), involving the three 4-methyl-3,5-dinitrobenzenesulfonate groups and the $\text{H}_2\text{O}\cdots\text{H}_3\text{O}^+$ group.

Experimental

1,2,3,5-Tetramethylpyrazolium 4-toluenesulfonate was prepared from 1,3,5-trimethylpyrazine and methyl 4-toluenesulfonate following a similar procedure as used for 1,2,3,5-trimethyl-4-nitropyrazolium 4-toluenesulfonate (Burton, *et al.*, 1971). Nitration of 1,2,3,5-tetramethylpyrazolium 4-toluenesulfonate was carried out under similar conditions used for 4-toluenesulfonyl chloride (Schmidt *et al.*, 1999). The title compound was obtained by recrystallization from EtOH of the product isolated on careful addition of the reaction mixture to ice (m.p. 330–332 K).

Crystal data

$2\text{C}_7\text{H}_{12}\text{N}_3\text{O}_2^+\cdot\text{H}_5\text{O}_2^+\cdot 3\text{C}_7\text{H}_5\text{N}_2\text{O}_7\text{S}^-$
 $M_r = 1161.00$
 Monoclinic, $P2_1/c$
 $a = 26.0927(5) \text{ \AA}$
 $b = 8.17230(10) \text{ \AA}$
 $c = 24.0602(6) \text{ \AA}$
 $\beta = 106.7241(8)^\circ$
 $V = 4913.52(17) \text{ \AA}^3$
 $Z = 4$

$D_x = 1.569 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 10634 reflections
 $\theta = 2.9\text{--}27.5^\circ$
 $\mu = 0.26 \text{ mm}^{-1}$
 $T = 120(2) \text{ K}$
 Slab, colourless
 $0.45 \times 0.20 \times 0.04 \text{ mm}$

Data collection

Bruker–Nonius KappaCCD diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
 $T_{\min} = 0.834$, $T_{\max} = 0.990$
 53726 measured reflections

11088 independent reflections
 8214 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.044$
 $\theta_{\max} = 27.5^\circ$
 $h = -33 \rightarrow 33$
 $k = -10 \rightarrow 10$
 $l = -29 \rightarrow 31$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.050$
 $wR(F^2) = 0.145$
 $S = 1.06$
 11088 reflections
 732 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0891P)^2 + 0.908P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.55 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.59 \text{ e \AA}^{-3}$
 Extinction correction: SHELXL97
 Extinction coefficient: 0.0067(5)

Table 1

Hydrogen-bond geometry (\AA , $^\circ$).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{O2}-\text{H2C}\cdots\text{O1}$	1.02(5)	1.42(5)	2.433(3)	176(4)
$\text{O1}-\text{H1A}\cdots\text{O541}$	0.83(4)	1.85(4)	2.681(3)	176(4)
$\text{O1}-\text{H1B}\cdots\text{O341}$	0.90(3)	1.79(4)	2.690(2)	173(3)
$\text{O2}-\text{H2A}\cdots\text{O441}^{\text{i}}$	0.95(3)	1.64(4)	2.570(2)	164(3)
$\text{O2}-\text{H2B}\cdots\text{O342}^{\text{ii}}$	0.87(3)	1.73(3)	2.590(2)	170(3)
$\text{C43}-\text{H43}\cdots\text{O462}^{\text{iii}}$	0.95	2.46	3.401(3)	172
$\text{C55}-\text{H55}\cdots\text{O342}^{\text{ii}}$	0.95	2.55	3.212(3)	127

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

H atoms were located in difference maps and, except for those in the H₅O₂ group, were then treated as riding atoms, with C–H distances of 0.95 (aromatic) or 0.96 Å (methyl) and *U*_{iso}(H) values of 1.2*U*_{eq}(aromatic C) or 1.5*U*_{eq}(methyl C). The existence and location of the additional H atom in the H₅O₂ group was demonstrated from a difference map (see *Comment*); all H atoms of this group were allowed to refine freely.

Data collection: *COLLECT* (Hooft, 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *OSCAIL* (McArdle, 2003) and *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

We are indebted to the EPSRC for the use of both the Chemical Database Service at Daresbury, England (Fletcher *et al.*, 1996), primarily for access to the Cambridge Structural Database, and the X-ray service at the University of Southampton, England, for data collection. We thank CNPq, Brazil, for financial support.

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