

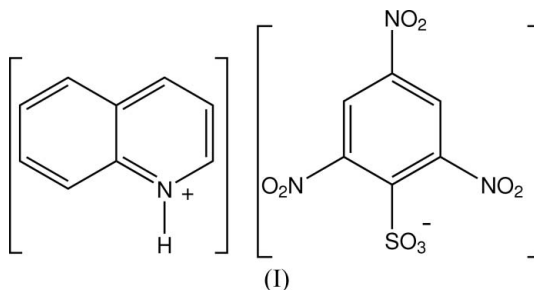
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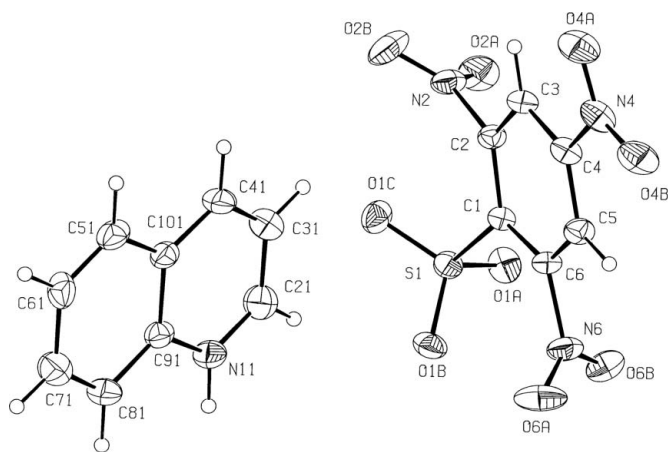
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## Key indicators

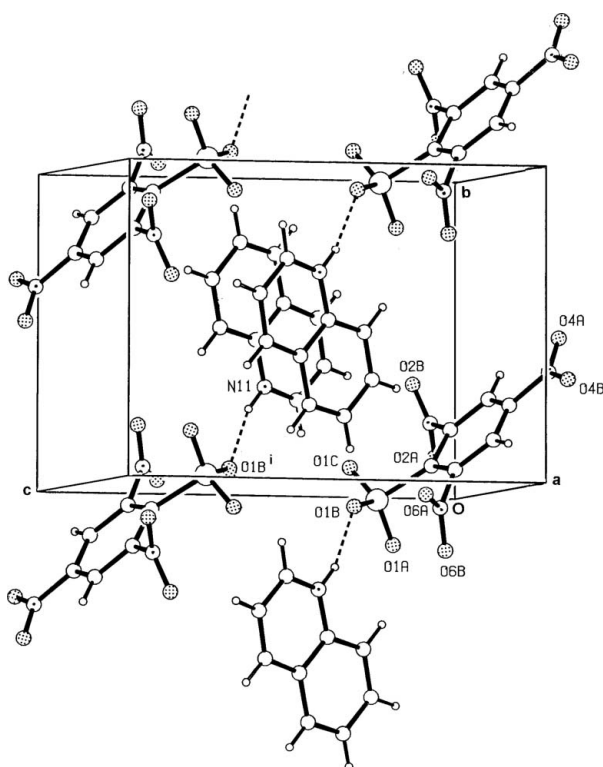
Single-crystal X-ray study  
 $T = 297$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.004$  Å  
 $R$  factor = 0.038  
 $wR$  factor = 0.111  
Data-to-parameter ratio = 11.4For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.Anhydrous quinolinium 2,4,6-trinitro-  
benzenesulfonateThe title compound,  $\text{C}_9\text{H}_8\text{N}^+\cdot\text{C}_6\text{H}_2\text{N}_3\text{O}_9\text{S}^-$  forms a simple dimer structure through a single  $\text{N}^+-\text{H}\cdots\text{O}$  hydrogen bond involving a sulfonate O atom of the cation. Some cation-cation  $\pi-\pi$  interactions are also present.Received 24 October 2006  
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## Comment

Quinoline ( $\text{p}K_{\text{a}} = 4.8$ ) can be readily protonated by sulfonic acids as well as by many carboxylic acids. The single  $\text{N}^+-\text{H}$  donor group of the resultant quinolinium cation is not a particularly efficient one for molecular assembly *via* hydrogen bonding. However, cation-cation or cation-anion  $\pi-\pi$  associations together with aromatic  $\text{C}-\text{H}\cdots\text{O}$  interactions are often present in the structures of quinolinium compounds with aromatic carboxylic acids that give stable crystalline materials, *e.g.* in the anhydrous salt with 3,5-dinitrosalicylic acid (Smith *et al.*, 2006). With aromatic sulfonic acids, the presence of the additional O acceptor atom of the sulfonate group usually results in the incorporation of donor-rich solvent molecules such as water in the crystal structure, *e.g.* quinolinium 5-sulfosalicylate trihydrate (Smith *et al.*, 2004). Therefore, the formation of the title compound, (I), from the 1:1 stoichiometric reaction of quinoline with picrylsulfonic acid in 50% propan-2-ol-water was unusual and its structure is reported here.In compound (I) (Fig. 1), the quinolinium H atom has a single interaction with a sulfonate-O acceptor of the anion [ $\text{N}11-\text{H}11\cdots\text{O}1\text{B}^i = 2.725(3)$  Å and  $\text{N}-\text{H}\cdots\text{O} = 162(2)^\circ$ ; symmetry code: (i)  $-x + 1, -y, -z + 1$ ], giving a simple hydrogen-bonded heterodimer. The quinolinium cations form stacks through alternating inversion-related molecules in the unit cell (Fig. 2) [ring centroid separation =  $3.666(2)$  Å; inter-ring dihedral angle =  $0^\circ$ ]. The second and third sulfonate O atoms and the six nitro-O atoms are unassociated except for minor weak  $\text{C}-\text{H}\cdots\text{O}$  interactions [ $\text{C}21-\text{H}\cdots\text{O}1\text{B} = 3.342(4)$  Å,  $\text{C}81-\text{H}\cdots\text{O}1\text{A}^i = 3.466(3)$  Å and  $\text{C}5-\text{H}\cdots\text{O}2\text{A}^{ii} = 3.241(4)$  Å; symmetry code: (ii)  $x + 1, y, z$ ]. An



**Figure 1**  
The asymmetric unit of (I). Displacement ellipsoids are drawn at the 30% probability level.



**Figure 2**  
A perspective view of the packing in the unit cell of (I), viewed approximately down the *a*-axis direction, showing hydrogen-bonded associations as dashed lines. [Symmetry code (i):  $-x + 1, -y, -z + 1$ ].

unusually short non-bonding intermolecular sulfonate- $O \cdots$ nitro-N interaction is also present [O1A $\cdots$ N4<sup>iii</sup> = 2.840 (3) Å; symmetry code: (iii)  $-x + 1, y, z$ ].

The *ortho*-related nitro groups of the picrylsulfonate anions are significantly rotated out of the plane of the benzene ring [torsion angles C1–C2–N2–O2A =  $-61.6$  (3)° and C1–C6–N6–O6B =  $61.6$  (3)°] compared with the essentially coplanar *para*-related group [C3–C4–N4–O4B =  $-176.8$  (3)°].

## Experimental

The title compound was synthesized by heating together 2,4,6-trinitrobenzenesulfonic acid (picrylsulfonic acid) (1 mmol) and quinoline (1 mmol) in 50% propan-2-ol–water (50 ml) under reflux for 10 min. After concentration to *ca* 30 ml, partial room-temperature evaporation of the hot-filtered solution gave yellow crystal plates (m.p. 532.7–533.9 K).

### Crystal data

$C_9H_8N^+ \cdot C_6H_2N_3O_9S^-$   
 $M_r = 422.33$   
Triclinic,  $P\bar{1}$   
 $a = 8.1070$  (19) Å  
 $b = 9.486$  (2) Å  
 $c = 12.581$  (2) Å  
 $\alpha = 79.41$  (2)°  
 $\beta = 82.347$  (16)°  
 $\gamma = 64.909$  (16)°

$V = 859.6$  (3) Å<sup>3</sup>  
 $Z = 2$   
 $D_x = 1.632$  Mg m<sup>-3</sup>  
Mo  $K\alpha$  radiation  
 $\mu = 0.25$  mm<sup>-1</sup>  
 $T = 297$  (2) K  
Plate, yellow  
 $0.36 \times 0.28 \times 0.11$  mm

### Data collection

Rigaku AFC 7R diffractometer  
 $\omega/2\theta$  scans  
Absorption correction:  $\psi$  scan  
TEXSAN for Windows (Molecular Structure Corporation, 1999)  
 $T_{\min} = 0.90, T_{\max} = 0.97$   
3552 measured reflections

3026 independent reflections  
1992 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.017$   
 $\theta_{\max} = 25.0^\circ$   
3 standard reflections  
frequency: 150 min  
intensity decay: 0.5%

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.038$   
 $wR(F^2) = 0.111$   
 $S = 0.95$   
3026 reflections  
266 parameters  
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0556P)^2 + 0.1982P]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.18$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.30$  e Å<sup>-3</sup>

The single quinolinium H atom was located by difference methods and its positional and isotropic displacement parameters were refined [refined N–H = 0.89 (3) Å]. The aromatic ring H atoms were included in the refinement in calculated positions, with C–H = 0.95 Å, and treated using a riding-model approximation, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ .

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1999); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* for Windows (Molecular Structure Corporation, 1999); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *PLATON*.

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