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Key indicators

Single-crystal X-ray study

$T = 297\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.004\text{ \AA}$

R factor = 0.038

wR factor = 0.111

Data-to-parameter ratio = 11.4

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

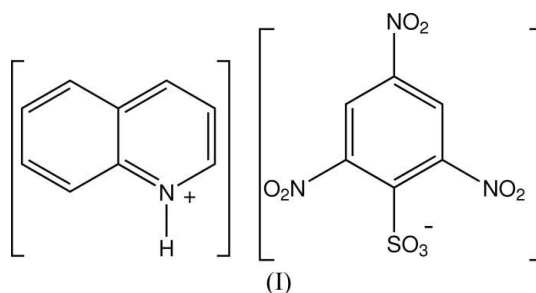
Anhydrous quinolinium 2,4,6-trinitrobenzenesulfonate

The 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.

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Comment

Quinoline ($\text{p}K_a = 4.8$) can be readily protonated by sulfonic acids as well as by many carboxylic acids. The single N^+-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 [$\text{N11}-\text{H11}\cdots\text{O1B}^i = 2.725(3)\text{ \AA}$ 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 = $3.666(2)\text{ \AA}$; inter-ring dihedral angle = 0°]. 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 [$\text{C21}-\text{H}\cdots\text{O1B} = 3.342(4)\text{ \AA}$, $\text{C81}-\text{H}\cdots\text{O1A}^i = 3.466(3)\text{ \AA}$ and $\text{C5}-\text{H}\cdots\text{O2A}^{ii} = 3.241(4)\text{ \AA}$; symmetry code: (ii) $x + 1, y, z$]. An

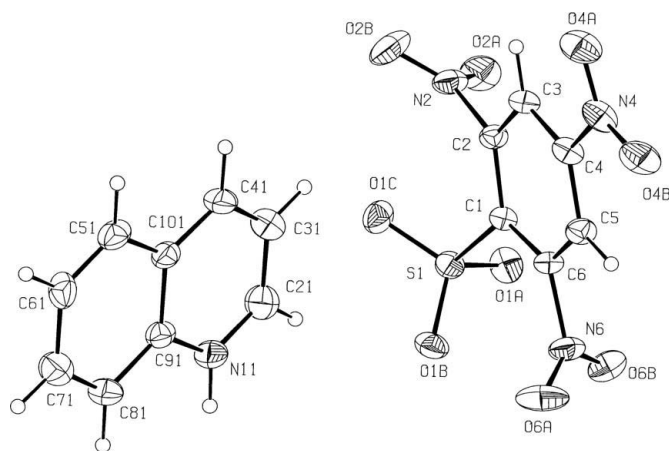


Figure 1
The asymmetric unit of (I). Displacement ellipsoids are drawn at the 30% probability level.

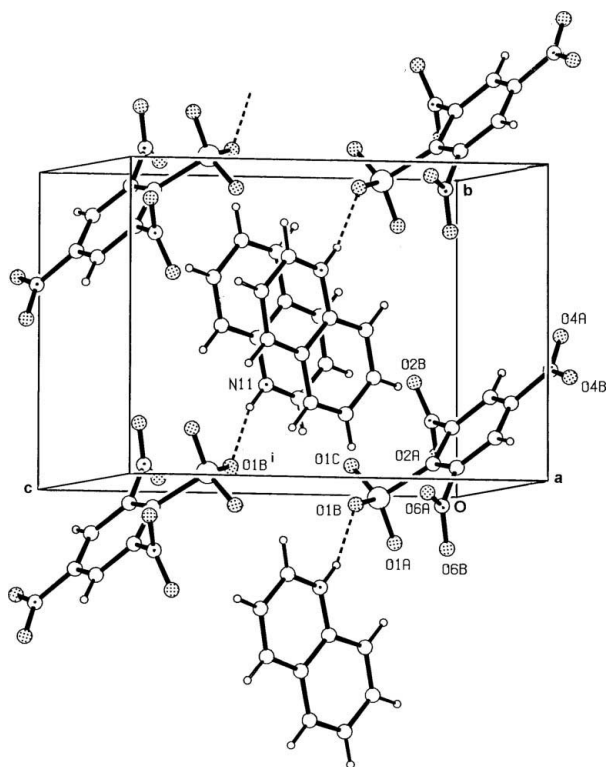


Figure 2
A perspective view of the packing in the unit cell of (I), viewed approximately down the *a*-axis direction, showing hydrogen-bonded associations as dashed lines. [Symmetry code (i): $-x + 1, -y, -z + 1$.]

unusually short non-bonding intermolecular sulfonate- $\text{O} \cdots \text{nitro-N}$ interaction is also present [$\text{O1A} \cdots \text{N4}^{\text{iii}} = 2.840(3) \text{ \AA}$; 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 $\text{C1-C2-N2-O2A} = -61.6(3)^\circ$ and $\text{C1-C6-N6-O6B} = 61.6(3)^\circ$] compared with the essentially coplanar *para*-related group [$\text{C3-C4-N4-O4B} = -176.8(3)^\circ$].

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

$\text{C}_9\text{H}_8\text{N}^+ \cdot \text{C}_6\text{H}_2\text{N}_3\text{O}_9\text{S}^-$
 $M_r = 422.33$
 Triclinic, $P\bar{1}$
 $a = 8.1070(19) \text{ \AA}$
 $b = 9.486(2) \text{ \AA}$
 $c = 12.581(2) \text{ \AA}$
 $\alpha = 79.41(2)^\circ$
 $\beta = 82.347(16)^\circ$
 $\gamma = 64.909(16)^\circ$

$V = 859.6(3) \text{ \AA}^3$
 $Z = 2$
 $D_x = 1.632 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 $\mu = 0.25 \text{ mm}^{-1}$
 $T = 297(2) \text{ K}$
 Plate, yellow
 $0.36 \times 0.28 \times 0.11 \text{ mm}$

Data collection

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

3026 independent reflections
 1992 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.017$
 $\theta_{\text{max}} = 25.0^\circ$
 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 $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.18 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.30 \text{ e \AA}^{-3}$

The single quinolinium H atom was located by difference methods and its positional and isotropic displacement parameters were refined [refined N–H = $0.89(3) \text{ \AA}$]. The aromatic ring H atoms were included in the refinement in calculated positions, with C–H = 0.95 \AA , 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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