

Quinolin-8-aminium toluene-4-sulfonate

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Key indicators

Single-crystal X-ray study

T = 298 K

Mean $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$

R factor = 0.041

wR factor = 0.124

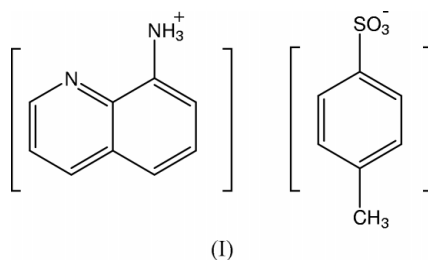
Data-to-parameter ratio = 16.6

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

The crystal structure of the 1:1 proton-transfer compound of 8-aminoquinoline with toluene-4-sulfonic acid, *viz.* quinolin-8-aminium toluene-4-sulfonate, $\text{C}_9\text{H}_9\text{N}_2^+ \cdot \text{C}_7\text{H}_7\text{O}_3\text{S}^-$, is different from previously characterized proton-transfer compounds of 8-aminoquinoline, in that the 8-amino group rather than the quinoline N atom is protonated. All H atoms of this aminium group are subsequently involved in intermolecular hydrogen-bonding interactions with sulfonate O-atom acceptors, linking the cationic and anionic species and forming a linear polymer structure.

Comment

8-Aminoquinoline (8-AQ) is stereochemically similar to 8-hydroxyquinoline (oxine = 8-HQ) and would appear to be as useful as 8-HQ for structure extension through hydrogen-bonding interactions. However, this is not the case, and only a small number of crystal structures of proton-transfer compounds of 8-AQ known, in contrast to those of 8-HQ (Smith, Wermuth & White, 2001). We have reported the crystal structures of the proton-transfer compounds of 8-AQ with a series of nitro-substituted carboxylic acids (Smith, Wermuth, Bott *et al.*, 2001) *viz.* 3-nitrobenzoic acid, 5-nitrosalicylic acid and 3,5-dinitrosalicylic acid (all 1:1), and chemically characterized those with 3,5-dinitrobenzoic acid (1:1) and 4-nitrobenzoic acid (a 1:1:1 acid adduct). In all of the crystal structures, 8-AQ adopts a bridging mode *via* the quinolinium- and amino-nitrogen groups, linking the acid molecules into linear chains. A 1:1 adduct with Kemp's triacid (*cis,cis*-1,3,5-trimethylcyclohexane-1,3,5-tricarboxylic acid) (Smith *et al.*, 2000) is surprisingly not a proton-transfer complex, considering the acid strength ($\text{p}K_{\text{a}1} = 1.5$). An unstable disordered adduct with 1,3,5-trinitrobenzene (TNB), with the formula $[(8\text{-AQ})_{0.8}(\text{TNB})_{0.6}]$, is also known (Smith, Wermuth, Bott *et al.*, 2001).



The structure of only one compound with a sulfonic acid, 5-sulfosalicylic acid (a 1:1 dihydrate), is known (Smith, Wermuth, Healy & White, 2004), so we undertook the preparation of crystals of 8-AQ salts with a series of aromatic sulfonic acids, with the aim of characterizing the hydrogen-

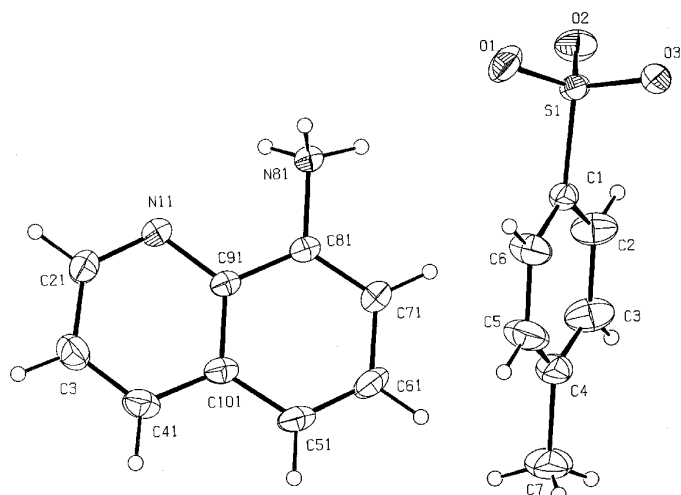


Figure 1

The molecular configuration and atom-numbering scheme for the 8-AQ cation and PTSA anion in (I). Displacement ellipsoids are drawn at the 30% probability level.

bonding patterns in such compounds, but without much success. One exception was the 1:1 proton-transfer compound with 4-toluenesulfonic acid (PTSA), (I), reported here. Success with PTSA is unusual, considering that crystal structures of proton-transfer Lewis base compounds with PTSA are uncommon, possibly because of the absence of interactive secondary substituent functional groups to promote hydrogen-bonding extension.

The structure determination of (I) shows, as expected, the presence of proton transfer but, surprisingly, the acceptor is the 8-amino substituent group rather than the quinoline hetero-N atom, as has been observed in all previous examples involving quinoline or substituted quinolines and strong aromatic carboxylic acids (Smith, Wermuth, Bott *et al.*, 2001; Smith, Wermuth, Healy & White, 2004) or aromatic sulfonic acids (Smith, Wermuth & White, 2004). It was assumed, in the absence of pK_a data for the second dissociation constant for 8-AQ ($pK_{a1} = 4.0$ *cf.* 4.8 for the hetero-N atom of quinoline) that the amino-N atom was less basic and should be protonated last. However, the difference may not be great and the reason for the phenomenon reported here may be that there is a stereochemical advantage in the association provided by the protonated primary amine group rather than the hetero-N atom.

Fig. 1 shows the 8-AQ cation and PTSA anion pair in (I). In (I), all three hydrogen donors of the protonated amine group give direct hydrogen-bonding associations, with two of the sulfonate O-atom acceptors from three independent PTSA anions [$N \cdots O$ distances: $N81 \cdots O3^i = 2.800$ (2), $N81 \cdots O3^{ii} = 2.868$ (2) and $N81 \cdots O1^{iii} = 2.791$ (3) Å; symmetry codes: (i) $x, 1 + y, z - 1$; (ii) $1 - x, 1 - y, 1 - z$; (iii) $1 + x, 1 + y, z - 1$]. The third sulfonate O atom (O2) is not involved, nor is the hetero-N atom (N11). In this respect, the 8-AQ molecule behaves in a very different manner from that found in previous structures, where it acts as a bidentate extender. The aminium group hydrogen-bonding associations in (I) are the only ones present in the structure, apart from the homo-

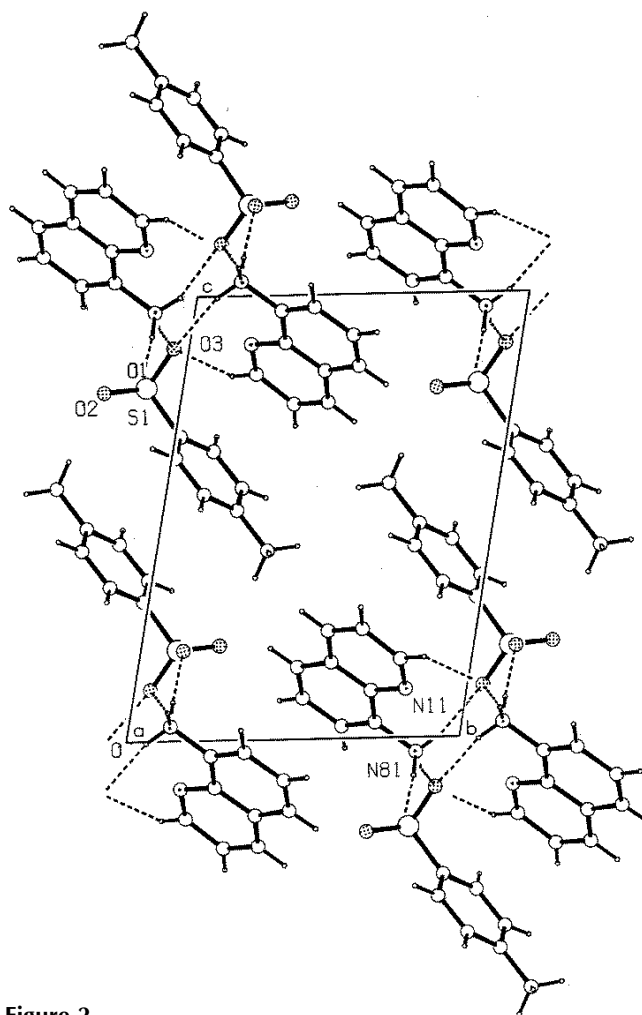


Figure 2

The packing of (I) in the unit cell, viewed down a , showing hydrogen-bonding associations as dashed lines.

molecular π - π stacking of the six-membered C51–C101 portions of the centrosymmetrically related 8-AQ cation rings [perpendicular separation = 3.38 (1) Å; $Cg \cdots Cg = 3.72$ (1) Å]. These result in a linear polymer structure extending along the a axis (Fig. 2).

Experimental

The synthesis of the title compound was carried out by refluxing 1 mmol quantities of 8-aminoquinoline (8-AQ) and toluene-4-sulfonic acid (PTSA) in 50 ml of 80% ethanol/water for 10 min. After concentration to *ca* 30 ml, partial room-temperature evaporation of the hot-filtered solution gave colourless prismatic crystals (m.p. 421.5–425.0 K).

Crystal data

$C_9H_9N_2^+ \cdot C_7H_7O_3S^-$
 $M_r = 316.37$
 Triclinic, $P\bar{1}$
 $a = 6.0986$ (14) Å
 $b = 9.8930$ (17) Å
 $c = 13.424$ (2) Å
 $\alpha = 78.11$ (15)°
 $\beta = 79.217$ (16)°
 $\gamma = 78.599$ (14)°
 $V = 767.8$ (4) Å³

$Z = 2$
 $D_x = 1.368$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 12.6$ – 17.4 °
 $\mu = 0.22$ mm⁻¹
 $T = 298$ (2) K
 Prism, colourless
 $0.40 \times 0.20 \times 0.18$ mm

Data collection

| | |
|--|------------------------------|
| Rigaku AFC-7R diffractometer | $\theta_{\max} = 27.5^\circ$ |
| ω - 2θ scans | $h = -7 \rightarrow 3$ |
| Absorption correction: none | $k = -12 \rightarrow 12$ |
| 4042 measured reflections | $l = -17 \rightarrow 17$ |
| 3528 independent reflections | 3 standard reflections |
| 2857 reflections with $I > 2\sigma(I)$ | every 150 reflections |
| $R_{\text{int}} = 0.031$ | intensity decay: 0.4% |

Refinement

| | |
|--|--|
| Refinement on F^2 | $w = 1/[\sigma^2(F_o^2) + (0.1P)^2 + 2.0104P]$ |
| $R[F^2 > 2\sigma(F^2)] = 0.042$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $wR(F^2) = 0.124$ | $(\Delta/\sigma)_{\max} < 0.001$ |
| $S = 0.83$ | $\Delta\rho_{\max} = 0.28 \text{ e } \text{\AA}^{-3}$ |
| 3528 reflections | $\Delta\rho_{\min} = -0.29 \text{ e } \text{\AA}^{-3}$ |
| 212 parameters | Extinction correction: <i>SHELXL97</i> |
| H atoms treated by a mixture of independent and constrained refinement | Extinction coefficient: 0.019 (3) |

Table 1

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

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|-------------------------------------|----------|-------------|-------------|---------------|
| N81—H81A \cdots O3 ⁱ | 0.95 (2) | 1.86 (2) | 2.800 (2) | 168.6 (18) |
| N81—H81B \cdots O3 ⁱⁱ | 0.88 (3) | 2.14 (3) | 2.868 (2) | 140 (2) |
| N81—H81C \cdots O1 ⁱⁱⁱ | 0.97 (3) | 1.83 (3) | 2.791 (3) | 169 (3) |
| C21—H21 \cdots O3 ^{iv} | 0.96 | 2.59 | 3.494 (3) | 158 |

Symmetry codes: (i) $x, 1+y, z-1$; (ii) $1-x, 1-y, 1-z$; (iii) $1+x, 1+y, z-1$; (iv) $2-x, 1-y, 1-z$.

H atoms of the protonated amine group of 8-AQ (H81A–C) were located by difference methods and their positional and isotropic displacement parameters were refined. Others were included in the

refinement at calculated positions ($C-H = 0.96 \text{ \AA}$) as riding models 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: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON for Windows* (Spek, 1999); software used to prepare material for publication: *PLATON for Windows*.

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