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4-Nitroanilinium *p*-toluenesulfonate

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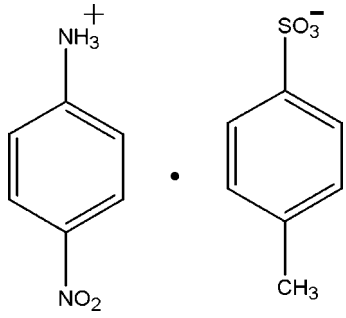
Key indicators: single-crystal X-ray study; T = 295 K; mean σ(C–C) = 0.004 Å; R factor = 0.053; wR factor = 0.134; data-to-parameter ratio = 18.3.

In the cation of the title salt, $C_6H_7N_2O_2^+\cdot C_7H_7O_3S^-$, the benzene ring makes a dihedral angle of 10.2 (2)° with the nitro group. In the crystal, the cations and anions are linked by weak N—H···O hydrogen bonds, forming a layer parallel to the *ac* plane. A weak C—H···O interaction and π–π interactions [centroid–centroid distances of 3.738 (3) and 3.748 (3) Å] also observed within the layer.

Related literature

For related structures of 4-toluenesulfonate salts, see: Koshima *et al.* (2004); Biradha & Mahata (2005). For bond-length data, see: Allen *et al.* (1987).



Experimental

Crystal data

$C_6H_7N_2O_2^+\cdot C_7H_7O_3S^-$
M_r = 310.32
Monoclinic, $P2_1/n$
a = 6.216 (5) Å
b = 30.674 (4) Å
c = 7.405 (5) Å
β = 97.048 (5)°
V = 1401.2 (15) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.26 mm^{-1}
T = 295 K
0.30 × 0.24 × 0.20 mm

Data collection

Bruker Kappa APEXII diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.928, T_{max} = 0.951
13942 measured reflections
3509 independent reflections
3232 reflections with $I > 2\sigma(I)$
R_{int} = 0.024

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.053
$wR(F^2)$ = 0.134
S = 1.22
3509 reflections
192 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.54 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N2—H14*B*···O3	0.89	2.09	2.856 (3)	144
N2—H14*A*···O2^{i}	0.89	2.07	2.961 (3)	175
N2—H14*B*···O1^{ii}	0.89	2.33	2.801 (3)	113
N2—H14*C*···O2^{iii}	0.89	1.96	2.834 (3)	167
C12—H12···O3^{iv}	0.93	2.59	3.193 (3)	123

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

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IS5199).

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supporting information

Acta Cryst. (2012). E**68**, o3059 [https://doi.org/10.1107/S1600536812040664]

4-Nitroanilinium *p*-toluenesulfonate

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S1. Comment

The asymmetric unit of the title compound (Fig. 1) contains one $C_6H_7N_2O_2^+$ cation and one $C_7H_7O_3S^-$ anion. The bond lengths and angles in both anion and cation are within normal range (Allen *et al.*, 1987) and those in the anion are comparable to those in other 4-toluenesulfonate salts (Koshima *et al.*, 2004; Biradha & Mahata, 2005). The crystal structure exhibit weak intermolecular N—H···O and C—H···O hydrogen bonds (Table 1 & Fig. 2) and π–π interactions. [*Cg*1···*Cg*2 (*x*, *y*, 1 + *z*) distance of 3.748 (3) Å; *Cg*2···*Cg*1 (*x*, *y*, -1 + *z*) distance of 3.748 (3) Å; *Cg*1···*Cg*2 (1/2 + *x*, 1/2 - *y*, 1/2 + *z*) distance of 3.738 (3) Å; *Cg*1 and *Cg*2 are the centroids of the rings (C1–C6) and (C8–C13), respectively.]

S2. Experimental

The title compound was formed from a mixture of 4-nitroaniline (2.15 g, 1 mmol) and p-toluenesulfonic acid (2.52 g, 1 mmol) in ethanol, which was stirred two hours at room temperature, giving a clear solution. After slow evaporation of ethanol for few days, single crystals suitable for X-ray diffraction were obtained.

S3. Refinement

H atoms were positioned geometrically and refined using riding model, with C—H = 0.93 Å and U_{iso}(H) = 1.2U_{eq}(C) for aromatic C—H, C—H = 0.96 Å and U_{iso}(H) = 1.5U_{eq}(C) for CH_3, and N—H = 0.89 Å and U_{iso}(H) = 1.5U_{eq}(N).

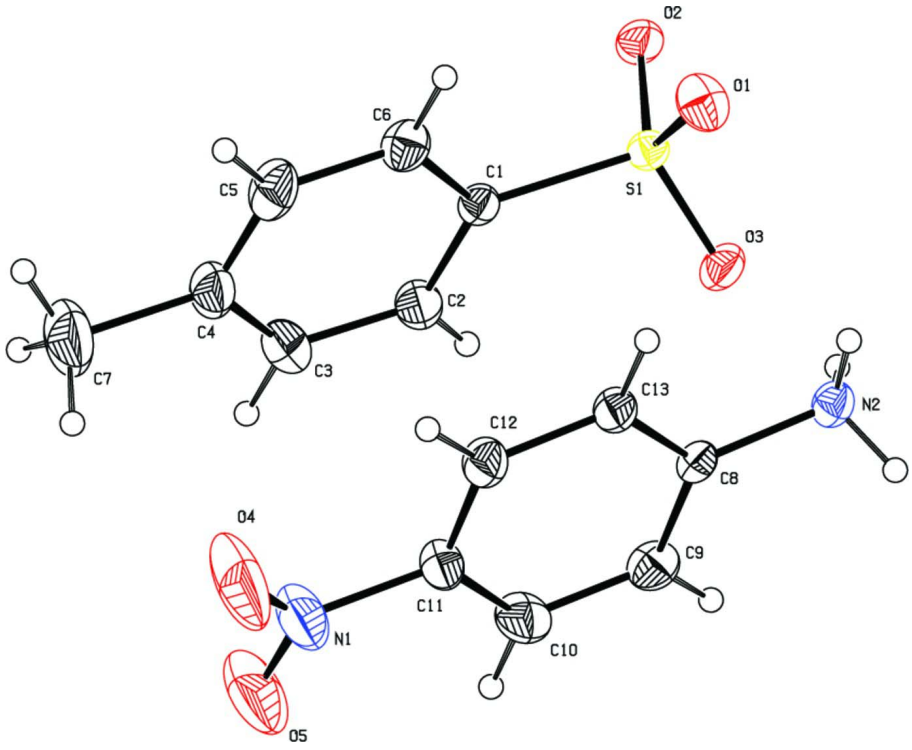

Figure 1

The molecular structure of the title compound, with atom labels and 30% probability displacement ellipsoids for non-H atoms.

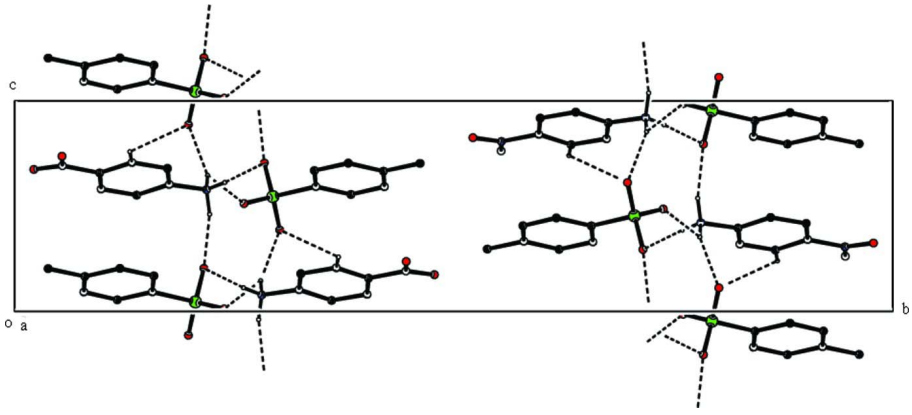

Figure 2

A packing diagram of the title compound, viewed down the *a* axis. Intermolecular hydrogen bonds are shown as dashed lines. H atoms not involved in hydrogen bonding have been omitted.

4-Nitroanilinium *p*-toluenesulfonate

Crystal data

$C_6H_7N_2O_2^+·C_7H_7O_3S^-$
M_r = 310.32
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn

a = 6.216 (5) Å
b = 30.674 (4) Å
c = 7.405 (5) Å
β = 97.048 (5)°

V = 1401.2 (15) Å^3
Z = 4
F(000) = 648
D_x = 1.471 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 4052 reflections

θ = 1.8–28.3°
μ = 0.26 mm^{-1}
T = 295 K
Block, colourless
0.30 × 0.24 × 0.20 mm

Data collection

Bruker Kappa APEXII diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω and φ scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.928, T_{max} = 0.951

13942 measured reflections
3509 independent reflections
3232 reflections with $I > 2\sigma(I)$
R_{int} = 0.024
θ_{max} = 28.4°, θ_{min} = 1.3°
h = −8→8
k = −41→35
l = −9→8

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.053
$wR(F^2)$ = 0.134
S = 1.22
3509 reflections
192 parameters
0 restraints
Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0471P)^2 + 0.984P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.54 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of F^2 > 2sigma(F^2) is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
C1	0.4464 (3)	0.15687 (6)	1.0932 (3)	0.0291 (4)
C2	0.3478 (4)	0.11695 (7)	1.0557 (3)	0.0413 (5)
H2	0.2032	0.1156	1.0056	0.050*
C3	0.4649 (5)	0.07893 (8)	1.0928 (4)	0.0526 (6)
H3	0.3974	0.0522	1.0676	0.063*
C4	0.6802 (5)	0.07991 (9)	1.1666 (4)	0.0513 (6)
C5	0.7754 (4)	0.11997 (9)	1.2045 (4)	0.0508 (6)
H5	0.9198	0.1212	1.2550	0.061*
C6	0.6614 (3)	0.15854 (8)	1.1694 (3)	0.0410 (5)
H6	0.7286	0.1852	1.1966	0.049*
C7	0.8092 (6)	0.03827 (11)	1.2035 (5)	0.0829 (11)

H7A	0.8506	0.0272	1.0914	0.124*
H7B	0.7220	0.0170	1.2558	0.124*
H7C	0.9369	0.0442	1.2866	0.124*
C8	0.4640 (3)	0.17612 (6)	0.6035 (2)	0.0287 (4)
C9	0.3447 (4)	0.13903 (8)	0.5530 (3)	0.0415 (5)
H9	0.2015	0.1413	0.5002	0.050*
C10	0.4402 (4)	0.09860 (8)	0.5817 (4)	0.0480 (6)
H10	0.3627	0.0732	0.5504	0.058*
C11	0.6539 (4)	0.09694 (7)	0.6584 (3)	0.0411 (5)
C12	0.7739 (4)	0.13364 (7)	0.7077 (3)	0.0400 (5)
H12	0.9177	0.1313	0.7590	0.048*
C13	0.6768 (3)	0.17402 (7)	0.6797 (3)	0.0345 (4)
H13	0.7543	0.1994	0.7118	0.041*
N2	0.3582 (3)	0.21852 (6)	0.5788 (2)	0.0328 (4)
H14A	0.4535	0.2395	0.6133	0.049*
H14B	0.2490	0.2198	0.6459	0.049*
H14C	0.3074	0.2221	0.4620	0.049*
N1	0.7608 (5)	0.05441 (7)	0.6924 (4)	0.0669 (7)
O1	0.4582 (3)	0.23868 (5)	1.0129 (3)	0.0461 (4)
O2	0.1910 (3)	0.21560 (5)	1.20530 (19)	0.0384 (3)
O3	0.1435 (2)	0.19798 (5)	0.8876 (2)	0.0379 (3)
O4	0.9550 (4)	0.05402 (8)	0.7374 (5)	0.1119 (12)
O5	0.6501 (5)	0.02194 (7)	0.6748 (5)	0.1009 (10)
S1	0.30084 (7)	0.205912 (15)	1.04561 (6)	0.02737 (14)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0279 (9)	0.0332 (9)	0.0263 (8)	0.0032 (7)	0.0039 (7)	0.0001 (7)
C2	0.0390 (11)	0.0364 (11)	0.0463 (12)	−0.0012 (9)	−0.0033 (9)	−0.0008 (9)
C3	0.0632 (16)	0.0345 (11)	0.0586 (15)	0.0043 (11)	0.0014 (12)	−0.0016 (10)
C4	0.0590 (15)	0.0487 (14)	0.0465 (13)	0.0220 (11)	0.0077 (11)	0.0053 (11)
C5	0.0343 (11)	0.0656 (16)	0.0509 (14)	0.0147 (11)	−0.0004 (10)	0.0083 (12)
C6	0.0308 (10)	0.0471 (12)	0.0436 (12)	−0.0005 (9)	−0.0018 (9)	0.0015 (9)
C7	0.091 (3)	0.066 (2)	0.091 (3)	0.0408 (19)	0.009 (2)	0.0157 (18)
C8	0.0280 (9)	0.0348 (9)	0.0230 (8)	0.0016 (7)	0.0020 (7)	0.0026 (7)
C9	0.0308 (10)	0.0482 (12)	0.0434 (12)	−0.0059 (9)	−0.0039 (9)	−0.0025 (10)
C10	0.0478 (13)	0.0388 (12)	0.0562 (14)	−0.0112 (10)	0.0016 (11)	−0.0054 (10)
C11	0.0472 (12)	0.0325 (10)	0.0434 (12)	0.0047 (9)	0.0053 (10)	0.0030 (9)
C12	0.0336 (10)	0.0402 (11)	0.0444 (12)	0.0040 (8)	−0.0032 (9)	0.0009 (9)
C13	0.0300 (9)	0.0341 (10)	0.0374 (10)	−0.0007 (8)	−0.0041 (8)	−0.0003 (8)
N2	0.0288 (8)	0.0389 (9)	0.0303 (8)	0.0044 (7)	0.0026 (6)	0.0028 (7)
N1	0.0780 (18)	0.0361 (11)	0.0860 (19)	0.0084 (11)	0.0073 (14)	0.0039 (11)
O1	0.0391 (8)	0.0369 (8)	0.0628 (11)	−0.0085 (6)	0.0081 (7)	0.0031 (7)
O2	0.0421 (8)	0.0455 (8)	0.0283 (7)	0.0105 (6)	0.0072 (6)	−0.0024 (6)
O3	0.0338 (7)	0.0469 (8)	0.0307 (7)	0.0050 (6)	−0.0053 (6)	0.0016 (6)
O4	0.0718 (17)	0.0540 (14)	0.203 (4)	0.0273 (12)	−0.0121 (19)	0.0111 (17)
O5	0.107 (2)	0.0358 (11)	0.156 (3)	−0.0028 (12)	0.0016 (19)	0.0068 (14)

S1	0.0253 (2)	0.0303 (2)	0.0264 (2)	−0.00042 (16)	0.00236 (16)	−0.00106 (16)

Geometric parameters (Å, º)

C1—C2	1.382 (3)	C9—C10	1.380 (3)
C1—C6	1.387 (3)	C9—H9	0.9300
C1—S1	1.768 (2)	C10—C11	1.380 (4)
C2—C3	1.384 (3)	C10—H10	0.9300
C2—H2	0.9300	C11—C12	1.375 (3)
C3—C4	1.383 (4)	C11—N1	1.472 (3)
C3—H3	0.9300	C12—C13	1.382 (3)
C4—C5	1.377 (4)	C12—H12	0.9300
C4—C7	1.515 (4)	C13—H13	0.9300
C5—C6	1.387 (3)	N2—H14A	0.8900
C5—H5	0.9300	N2—H14B	0.8900
C6—H6	0.9300	N2—H14C	0.8900
C7—H7A	0.9600	N1—O5	1.209 (3)
C7—H7B	0.9600	N1—O4	1.212 (4)
C7—H7C	0.9600	O1—S1	1.4436 (16)
C8—C13	1.374 (3)	O2—S1	1.4665 (16)
C8—C9	1.385 (3)	O3—S1	1.4507 (16)
C8—N2	1.459 (2)		
C2—C1—C6	119.73 (19)	C8—C9—H9	120.3
C2—C1—S1	120.68 (16)	C9—C10—C11	118.1 (2)
C6—C1—S1	119.59 (16)	C9—C10—H10	121.0
C1—C2—C3	119.8 (2)	C11—C10—H10	121.0
C1—C2—H2	120.1	C12—C11—C10	122.9 (2)
C3—C2—H2	120.1	C12—C11—N1	117.5 (2)
C4—C3—C2	121.3 (2)	C10—C11—N1	119.7 (2)
C4—C3—H3	119.3	C11—C12—C13	118.8 (2)
C2—C3—H3	119.3	C11—C12—H12	120.6
C5—C4—C3	118.1 (2)	C13—C12—H12	120.6
C5—C4—C7	120.7 (3)	C8—C13—C12	118.96 (19)
C3—C4—C7	121.2 (3)	C8—C13—H13	120.5
C4—C5—C6	121.7 (2)	C12—C13—H13	120.5
C4—C5—H5	119.1	C8—N2—H14A	109.5
C6—C5—H5	119.1	C8—N2—H14B	109.5
C1—C6—C5	119.3 (2)	H14A—N2—H14B	109.5
C1—C6—H6	120.3	C8—N2—H14C	109.5
C5—C6—H6	120.3	H14A—N2—H14C	109.5
C4—C7—H7A	109.5	H14B—N2—H14C	109.5
C4—C7—H7B	109.5	O5—N1—O4	123.8 (3)
H7A—C7—H7B	109.5	O5—N1—C11	118.2 (3)
C4—C7—H7C	109.5	O4—N1—C11	118.0 (2)
H7A—C7—H7C	109.5	O1—S1—O3	112.65 (11)
H7B—C7—H7C	109.5	O1—S1—O2	112.71 (10)
C13—C8—C9	121.95 (19)	O3—S1—O2	110.50 (11)

C13—C8—N2	119.34 (17)	O1—S1—C1	106.57 (10)
C9—C8—N2	118.70 (18)	O3—S1—C1	107.22 (9)
C10—C9—C8	119.4 (2)	O2—S1—C1	106.79 (9)
C10—C9—H9	120.3		

C6—C1—C2—C3	−0.6 (3)	C10—C11—C12—C13	0.0 (4)
S1—C1—C2—C3	179.55 (19)	N1—C11—C12—C13	−179.1 (2)
C1—C2—C3—C4	−0.2 (4)	C9—C8—C13—C12	−0.5 (3)
C2—C3—C4—C5	0.8 (4)	N2—C8—C13—C12	178.06 (18)
C2—C3—C4—C7	−178.8 (3)	C11—C12—C13—C8	0.0 (3)
C3—C4—C5—C6	−0.5 (4)	C12—C11—N1—O5	169.4 (3)
C7—C4—C5—C6	179.0 (3)	C10—C11—N1—O5	−9.8 (4)
C2—C1—C6—C5	0.8 (3)	C12—C11—N1—O4	−10.3 (4)
S1—C1—C6—C5	−179.28 (18)	C10—C11—N1—O4	170.6 (3)
C4—C5—C6—C1	−0.3 (4)	C2—C1—S1—O1	−152.38 (18)
C13—C8—C9—C10	0.9 (3)	C6—C1—S1—O1	27.7 (2)
N2—C8—C9—C10	−177.6 (2)	C2—C1—S1—O3	−31.5 (2)
C8—C9—C10—C11	−0.8 (4)	C6—C1—S1—O3	148.59 (17)
C9—C10—C11—C12	0.4 (4)	C2—C1—S1—O2	86.92 (19)
C9—C10—C11—N1	179.5 (2)	C6—C1—S1—O2	−92.96 (19)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H14*B*···O3	0.89	2.09	2.856 (3)	144
N2—H14*A*···O2^{i}	0.89	2.07	2.961 (3)	175
N2—H14*B*···O1^{ii}	0.89	2.33	2.801 (3)	113
N2—H14*C*···O2^{iii}	0.89	1.96	2.834 (3)	167
C12—H12···O3^{iv}	0.93	2.59	3.193 (3)	123

Symmetry codes: (i) *x*+1/2, −*y*+1/2, *z*−1/2; (ii) *x*−1/2, −*y*+1/2, *z*−1/2; (iii) *x*, *y*, *z*−1; (iv) *x*+1, *y*, *z*.