

2-Acetamido-4-*p*-tolyl-1,3-thiazole and 2-amino-4-*p*-tolyl-1,3-thiazolium chloride dihydrate

Daniel E. Lynch^{a*} and Ian McClenaghan^b

^aSchool of Science and the Environment, Coventry University, Coventry CV1 5FB, England, and ^bKey Organics Ltd, Highfield Industrial Estate, Camelford, Cornwall PL32 9QZ, England

Correspondence e-mail: apx106@coventry.ac.uk

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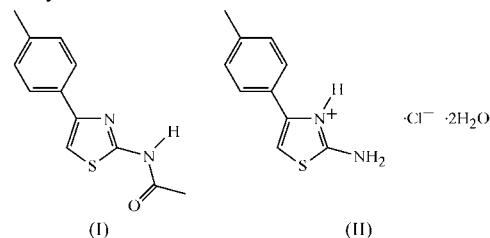
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The structures of 2-acetamido-4-*p*-tolyl-1,3-thiazole, C₁₂H₁₂N₂OS, (I), and 2-amino-4-*p*-tolyl-1,3-thiazolium chloride dihydrate, C₁₀H₁₁N₂S⁺·Cl⁻·2H₂O, (II), reveal that both molecules are essentially planar, with the respective dihedral angles between the benzene and thiazole rings being 2.9 (1) and 10.39 (7)°. Compound (I) associates *via* a single N—H···O interaction to form a flat alternate-facing hydrogen-bonded chain [graph-set C₂²(4)]. Compound (II) packs with the hydrogen-bonding associations of the Cl atoms and the water molecules creating a convoluted hydrogen-bonded ribbon made up of five-membered donor–acceptor rings, involving three water O atoms (with associated H atoms) and two Cl atoms. The thiazolium rings form stacked columns, aligned in the same direction as the hydrogen-bonded ribbons, of alternate-facing molecules that are also involved in the hydrogen-bonding network, linking to the Cl atoms and one of the water molecules. Subsequently, each Cl atom is the hydrogen-bond acceptor for five separate O/N—H associations.

Comment

2-Amino-4-phenyl-1,3-thiazole has both pharmaceutical and industrial applications (Au-Alvarez *et al.*, 1999), including corrosion inhibition (Form *et al.*, 1974); the structures of 2-amino-4-phenylthiazole and its hydrobromide hydrate salt are reported, respectively, in these two references. We have recently reviewed the structures of 2-amino-4-phenylthiazole derivatives in terms of their hydrogen-bonding patterns, specifically highlighting any involvement of the thiazole S atom (Lynch *et al.*, 2002). Since that paper, the structures of two more derivatives have been reported (Bernes *et al.*, 2002; Karanik *et al.*, 2003). Several of the analogues that we reported in 2002, such as 2-amino-4-*p*-tolyl-1,3-thiazole, either packed quite simply as hydrogen-bonded R₂²(8) graph-set (Etter, 1990) dimers through N—H···N interactions or displayed packing networks containing these dimers. In the cases where molecules did not associate *via* N—H···N

hydrogen bonds into dimers, and no other anions or water molecules were present, N—H···S interactions were observed. The molecular arrangements in both the Bernes *et al.* and Karanik *et al.* structures also included N—H···N dimers. As a continuation of our 2002 study into the packing modes of 2-amino-4-phenyl-1,3-thiazole derivatives, we have further determined the structures of 2-acetamido-4-*p*-tolyl-1,3-thiazole, (I), and 2-amino-4-*p*-tolyl-1,3-thiazolium chloride dihydrate, (II), and report them here. As seen in two structures discussed in our 2002 paper, the packing modes of 2-amino-4-phenyl-1,3-thiazoles with additional anions and/or water molecules differ from the structures of the thiazole molecules by themselves.



The structure of (I) consists of an essentially flat molecule (Fig. 1) which associates *via* a single N—H···O interaction, with alternate-facing molecules, to form a C₂²(4) graph-set hydrogen-bonded chain (Fig. 2). The N—H···O chain interaction (Table 1) is one of two typical motifs displayed by amide linkages, with the other being an N—H···O hydrogen-bonded R₂²(8) graph-set dimer (Desiraju, 1995). In other 2-acetamido-1,3-thiazole derivatives, of which there are four in the April 2004 version of the Cambridge Structural Database (CSD; Allen, 2002), none forms a hydrogen-bonded amide chain similar to (I). Instead, one, namely *N*-(5-nitro-2-thiazolyl)acetamide (Peeters *et al.*, 1985), forms an R₂²(8) N—H···N hydrogen-bonded dimer, while the other three structures contain additional lattice elements, such as anions, cations and/or water molecules. Furthermore, of 12 2-acetamido-1,3,4-thiadiazole derivatives found in the CSD, only one, namely 2-acetamido-4-benzoyl-5,5-dimethyl-4,5-dihydro-1,3,4-thiadiazoline (Kuban & Schulz, 1987), packs with a hydrogen-bonded amide chain. Interestingly, this molecule

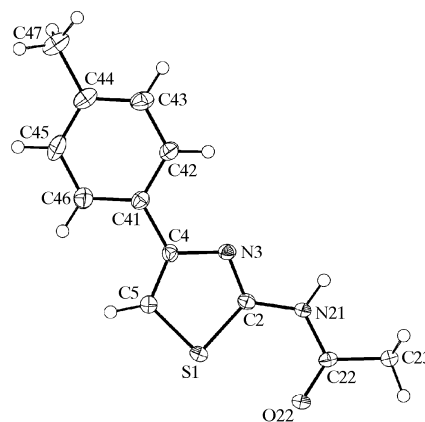


Figure 1

The molecular configuration and atom-numbering scheme for (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

contains a bulky substituent in the 4-position, similar to (I), whereas those molecules without such substituents predominantly pack as N—H···N dimers. In (I), the dihedral angle between the thiazole and phenyl rings is 2.9 (1)°. The comparative dihedral angle in 2-amino-4-tolylthiazole is 12.80 (8)°.

The structure of (II) consists of an essentially flat 2-amino-4-tolyl-1,3-thiazolium molecule, a Cl[−] anion and two water molecules (Fig. 3), associated in a hydrogen-bonded network. The CSD reveals that there are seven previously reported 2-amino-1,3-thiazolium halide (either Cl[−] or Br[−]) structures, with three of these being monohydrates; thus, (II) is unique in being the first reported dihydrate. In all of the reported structures, the halide anion associates with either N3 or N21, or both, although across these examples, all of the hydrate structures have N3⁺—H associating to a water O atom. Alternatively, in (II), the same Cl atom (details of hydrogen-bonding interactions are given in Table 2) associates with both N3 and N21, similar to the three non-hydrate structures, with the second H atom on N21 forming a hydrogen bond to a symmetry-equivalent water O atom [O1Wⁱⁱ, see Fig. 4; symmetry code: (ii) 1 − x, y − ½, −½ − z]. The Cl atom and the two water molecules associate *via* hydrogen-bonding interactions to construct a convoluted hydrogen-bonded ribbon network which runs in the *a* cell direction. This ribbon network is made up of five-membered donor–acceptor rings, involving three water O atoms (with associated H atoms) and two Cl atoms [Cl1, O1W, O2Wⁱⁱⁱ, Cl1ⁱⁱⁱ and O2W in Fig. 4; R₃⁵(10) graph set; symmetry code: (iii) x − ½, ½ − y, −z], fused along the O2W—H···Cl hydrogen bond. In addition to the hydrogen-

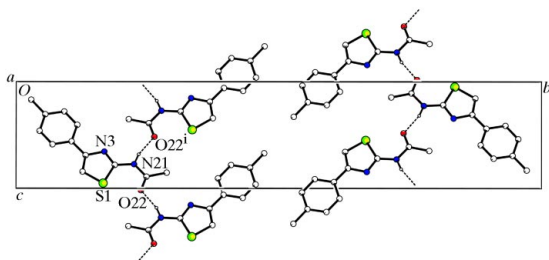


Figure 2
A packing diagram for (I), viewed down the *a* axis. [Symmetry code: (i) $x + \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$.]

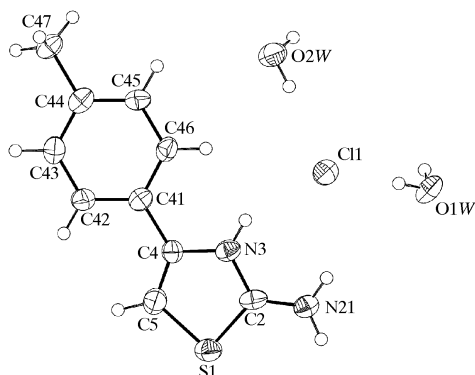


Figure 3
The molecular configuration and atom-numbering scheme for (II). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

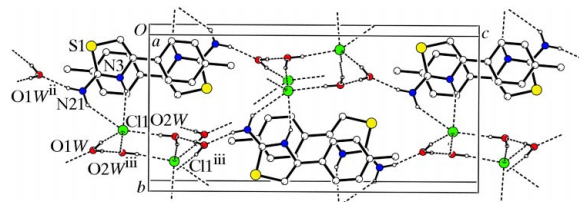


Figure 4
A packing diagram for (II). [Symmetry codes: (ii) 1 − x, y − ½, −½ − z; (iii) $x - \frac{1}{2}, \frac{3}{2} - y, -z$.]

bonding associations to Cl1 and O1W, the thiazolium molecules stack in a column co-directional with the anion–water ribbon. The thiazolium columns comprise alternate-facing molecules, with the perpendicular distances between thiazole–phenyl and phenyl–thiazole ring centroids being 3.60 (1) and 3.67 (1) Å, respectively, and with the closest contact distance being 3.35 (1) Å from C4···C42($x + \frac{1}{2}, \frac{1}{2} - y, -z$).

For (II), the dihedral angle between the thiazole and phenyl rings is 10.39 (7)°, which compares with a value of 19 (1)° for 2-amino-4-phenyl-1,3-thiazolium bromide hydrate (Form *et al.*, 1974) and 7.3 (2)° for 2-amino-4-naphthyl-1,3-thiazolium bromide (Lynch *et al.*, 2002). Also noteworthy in (II) is the indication of a delocalized double bond across the N3—C2—N21 site, with distances of 1.322 (8) (C2—N21) and 1.342 (8) Å (C2—N3), compared with distances of 1.351 (2) and 1.309 (2) Å, respectively, for 2-amino-4-tolylthiazole. Similar distances of 1.30 (2) and 1.33 (2) Å, respectively, for 2-amino-4-phenyl-1,3-thiazolium bromide hydrate, and 1.347 (5) and 1.298 (5) Å for 2-amino-4-phenyl-1,3-thiazole itself [the dihedral angle in this molecule is 6.2 (3)°] are also noted. The hydrogen-bonding coordination surrounding the Cl atom is interesting, because without the N21—H21···Cl1 association, the remaining four-coordinate motif is pseudo-tetrahedral, with the H···Cl···H angles from H3 being 94 (3), 118 (3) and 122 (3)°, and the three remaining angles being 105 (3), 105 (3) and 110 (3)°. The addition of the N21—H21···Cl1 association thus creates a five-coordinate pseudo-face-capped tetrahedral arrangement, not observed amongst the seven previously reported 2-amino-1,3-thiazolium halide structures.

Experimental

Both title compounds were obtained from Key Organics Ltd and crystals were grown from ethanol solutions. Data for (I) were collected at Station 9.8 of the Daresbury SRS (Cernik *et al.*, 1997; Clegg, 2000). Data for (II) were collected at the EPSRC Crystallographic Service, Southampton.

Compound (I)

Crystal data

C₁₂H₁₂N₂OS
M_r = 232.30
 Monoclinic, *P*₂₁/*n*
a = 3.9541 (5) Å
b = 37.484 (5) Å
c = 7.7173 (9) Å
 β = 99.338 (2)°
V = 1128.7 (2) Å³
Z = 4

D_x = 1.367 Mg m^{−3}
 Synchrotron radiation, λ = 0.6894 Å
 Cell parameters from 1753 reflections
 θ = 2.7–28.2°
 μ = 0.27 mm^{−1}
T = 120 (2) K
 Plate, colourless
 0.050 × 0.030 × 0.002 mm

Data collection

Bruker SMART 1K CCD area-detector diffractometer
 ω rotation scans with narrow frames
 6723 measured reflections
 2407 independent reflections
 1770 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.040$
 $\theta_{\text{max}} = 26.0^\circ$
 $h = -5 \rightarrow 2$
 $k = -44 \rightarrow 47$
 $l = -9 \rightarrow 9$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.049$
 $wR(F^2) = 0.126$
 $S = 1.08$
 2407 reflections
 151 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0604P)^2 + 0.4975P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.32 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.32 \text{ e } \text{\AA}^{-3}$

Table 1

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

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N21-H21 \cdots O22^i$	0.89 (3)	1.95 (3)	2.818 (3)	166 (3)

Symmetry code: (i) $\frac{1}{2} + x, \frac{1}{2} - y, z - \frac{1}{2}$.

Compound (II)

Crystal data

$C_{10}H_{11}N_2S^+ \cdot Cl^- \cdot 2H_2O$
 $M_r = 262.75$
 Orthorhombic, $P2_12_12_1$
 $a = 6.8815$ (6) \AA
 $b = 9.3072$ (14) \AA
 $c = 19.499$ (3) \AA
 $V = 1248.9$ (3) \AA^3
 $Z = 4$
 $D_x = 1.397 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation
 Cell parameters from 2244 reflections
 $\theta = 2.9-27.1^\circ$
 $\mu = 0.46 \text{ mm}^{-1}$
 $T = 120$ (2) K
 Needle, colourless
 $0.35 \times 0.02 \times 0.02 \text{ mm}$

Data collection

Nonius KappaCCD area-detector diffractometer
 φ and ω scans
 9123 measured reflections
 1441 independent reflections
 1048 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.156$
 $\theta_{\text{max}} = 26.0^\circ$
 $h = -8 \rightarrow 8$
 $k = -9 \rightarrow 11$
 $l = -23 \rightarrow 24$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.063$
 $wR(F^2) = 0.152$
 $S = 1.06$
 1441 reflections
 159 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0775P)^2 + 0.1085P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.44 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.47 \text{ e } \text{\AA}^{-3}$

All H atoms, except for the N—H atom in (I) and the water H atoms in (II), were included in the refinements at calculated positions in the riding-model approximation, with N—H distances of 0.88 \AA and C—H distances of 0.95 (aromatic H atoms) and 0.98 \AA (methyl H atoms), and with $U_{\text{iso}}(\text{H}) = 1.25U_{\text{eq}}(\text{C}, \text{N})$. The N—H atom in (I) was located in Fourier syntheses and both its positional and displacement parameters were refined. The water H atoms in (II) were also located in Fourier syntheses, but their positional and displacement parameters were refined with O—H distance restraints of 0.88 \AA and H \cdots H restraints of 1.4 \AA . $U_{\text{iso}}(\text{H})$ values for the water H atoms were

Table 2

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

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N3-H3 \cdots Cl1$	0.88	2.32	3.126 (5)	151
$N21-H21 \cdots Cl1$	0.88	2.58	3.337 (6)	144
$N21-H22 \cdots O1W^{ii}$	0.88	1.86	2.726 (7)	166
$O1W-H11W \cdots Cl1$	0.88 (6)	2.26 (6)	3.136 (5)	178 (7)
$O1W-H12W \cdots O2W^{iii}$	0.88 (5)	1.83 (3)	2.700 (7)	169 (8)
$O2W-H22W \cdots Cl1$	0.88 (2)	2.35 (2)	3.214 (5)	167 (6)
$O2W-H21W \cdots Cl1^{iii}$	0.88 (5)	2.29 (3)	3.151 (5)	166 (6)

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

set equal to $1.25U_{\text{eq}}(\text{O})$. Refinement of the absolute structure parameter (Flack, 1983) gave ambiguous results, indicating that the absolute structure of (II) could not be accurately determined from the diffraction data, even with the presence of a Cl atom; thus Friedel opposites were merged. For (II), the number of Friedel pairs is 837. The high R_{int} value was the result of weak high-angle data.

For compound (I), data collection, cell refinement and data reduction: *SMART* (Bruker, 2001). For compound (II), data collection and cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Nonius, 1998); data reduction: *DENZO*, *SCALEPACK* (Otwinowski & Minor, 1997) and *COLLECT*. For both compounds, program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA1090). Services for accessing these data are described at the back of the journal.

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supporting information

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2-Acetamido-4-*p*-tolyl-1,3-thiazole and 2-amino-4-*p*-tolyl-1,3-thiazolium chloride dihydrate

Daniel E. Lynch and Ian McClenaghan

Computing details

Data collection: *SMART* (Bruker, 2001) for (I); *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Nonius, 1998) for (II). Cell refinement: *SMART* for (I); *DENZO* and *COLLECT* for (II). Data reduction: *SMART* for (I); *DENZO*, *SCALEPACK* (Otwinowski & Minor, 1997) and *COLLECT* for (II). For both compounds, program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

(I) 2-Acetamido-4-*p*-tolyl-1,3-thiazole

Crystal data

C₁₂H₁₂N₂OS

$M_r = 232.30$

Monoclinic, $P2_1/n$

Hall symbol: -P 2yn

$a = 3.9541$ (5) Å

$b = 37.484$ (5) Å

$c = 7.7173$ (9) Å

$\beta = 99.338$ (2)°

$V = 1128.7$ (2) Å³

$Z = 4$

$F(000) = 488$

$D_x = 1.367$ Mg m⁻³

Synchrotron radiation, $\lambda = 0.6894$ Å

Cell parameters from 1753 reflections

$\theta = 2.7$ – 28.2 °

$\mu = 0.27$ mm⁻¹

$T = 120$ K

Plate, colourless

$0.05 \times 0.03 \times 0.002$ mm

Data collection

Bruker SMART 1K CCD area-detector diffractometer

Radiation source: Daresbury SRS Station 9.8

(Cernik et al., 1997; Clegg, 2000)

Silicon 111 monochromator

Detector resolution: 8.192 pixels mm⁻¹

ω rotation with narrow frames scans

6723 measured reflections

2407 independent reflections

1770 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.040$

$\theta_{\text{max}} = 26.0$ °, $\theta_{\text{min}} = 2.1$ °

$h = -5 \rightarrow 2$

$k = -44 \rightarrow 47$

$l = -9 \rightarrow 9$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.049$

$wR(F^2) = 0.126$

$S = 1.08$

2407 reflections

151 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 atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0604P)^2 + 0.4975P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$

$$\Delta\rho_{\max} = 0.32 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.32 \text{ e } \text{\AA}^{-3}$$

Special details

Geometry. Least-squares planes (x,y,z in crystal coordinates) and deviations from them (* indicates atom used to define plane)

$$3.4460 (0.0017) x - 2.8824 (0.0477) y + 2.5969 (0.0060) z = 3.7007 (0.0085)$$

$$* -0.0014 (0.0011) \text{ S1 } * -0.0004 (0.0014) \text{ C2 } * 0.0025 (0.0015) \text{ N3 } * -0.0039 (0.0016) \text{ C4 } * 0.0032 (0.0015) \text{ C5}$$

Rms deviation of fitted atoms = 0.0026

$$3.5389 (0.0021) x - 2.3368 (0.0465) y + 2.2430 (0.0086) z = 3.6065 (0.0047)$$

Angle to previous plane (with approximate e.s.d.) = 2.91 (0.13)

$$* -0.0026 (0.0019) \text{ C41 } * 0.0006 (0.0020) \text{ C42 } * 0.0028 (0.0021) \text{ C43 } * -0.0043 (0.0021) \text{ C44 } * 0.0023 (0.0022) \text{ C45 } * 0.0011 (0.0021) \text{ C46}$$

Rms deviation of fitted atoms = 0.0026

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.49456 (18)	0.165388 (17)	0.95180 (8)	0.02014 (19)
C2	0.6413 (6)	0.18746 (6)	0.7819 (3)	0.0175 (5)
N3	0.7199 (5)	0.16755 (5)	0.6567 (2)	0.0181 (4)
C4	0.6624 (7)	0.13189 (6)	0.6909 (3)	0.0180 (5)
C5	0.5445 (7)	0.12616 (7)	0.8438 (3)	0.0213 (6)
H5	0.4954	0.1033	0.8861	0.027*
N21	0.6790 (6)	0.22419 (5)	0.7745 (3)	0.0180 (5)
H21	0.761 (7)	0.2330 (7)	0.682 (4)	0.021 (7)*
C22	0.5850 (7)	0.24777 (7)	0.8913 (3)	0.0182 (5)
O22	0.4597 (5)	0.23738 (5)	1.0180 (2)	0.0229 (4)
C23	0.6423 (7)	0.28629 (6)	0.8541 (3)	0.0205 (5)
H231	0.5667	0.3010	0.9454	0.026*
H232	0.5110	0.2926	0.7394	0.026*
H233	0.8868	0.2904	0.8531	0.026*
C41	0.7322 (7)	0.10513 (6)	0.5611 (3)	0.0200 (5)
C42	0.8383 (8)	0.11578 (7)	0.4062 (3)	0.0261 (6)
H42	0.8681	0.1405	0.3852	0.033*
C43	0.9016 (8)	0.09101 (8)	0.2815 (4)	0.0282 (6)
H43	0.9750	0.0990	0.1769	0.035*
C44	0.8595 (7)	0.05489 (8)	0.3072 (4)	0.0284 (6)
C45	0.7557 (8)	0.04429 (7)	0.4627 (4)	0.0341 (7)
H45	0.7277	0.0196	0.4837	0.043*
C46	0.6919 (8)	0.06869 (7)	0.5884 (4)	0.0283 (6)
H46	0.6204	0.0606	0.6934	0.035*
C47	0.9250 (9)	0.02808 (8)	0.1707 (4)	0.0402 (8)
H471	1.1704	0.0226	0.1861	0.050*
H472	0.8508	0.0380	0.0532	0.050*
H473	0.7963	0.0062	0.1842	0.050*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0254 (4)	0.0209 (3)	0.0154 (3)	-0.0006 (3)	0.0069 (2)	0.0009 (2)
C2	0.0183 (13)	0.0202 (12)	0.0133 (11)	0.0005 (10)	0.0004 (9)	0.0012 (9)
N3	0.0205 (11)	0.0192 (10)	0.0145 (9)	0.0015 (9)	0.0026 (8)	-0.0003 (8)
C4	0.0202 (13)	0.0161 (12)	0.0170 (11)	-0.0001 (10)	0.0007 (10)	0.0008 (9)
C5	0.0270 (15)	0.0178 (12)	0.0195 (12)	-0.0007 (11)	0.0050 (11)	0.0001 (10)
N21	0.0240 (12)	0.0176 (10)	0.0134 (10)	0.0002 (9)	0.0061 (9)	0.0004 (8)
C22	0.0194 (13)	0.0207 (12)	0.0146 (11)	0.0017 (10)	0.0030 (10)	-0.0028 (9)
O22	0.0320 (11)	0.0223 (9)	0.0166 (9)	0.0003 (8)	0.0108 (8)	-0.0004 (7)
C23	0.0255 (14)	0.0184 (12)	0.0187 (12)	-0.0001 (10)	0.0066 (10)	-0.0011 (10)
C41	0.0201 (13)	0.0196 (13)	0.0193 (12)	0.0004 (10)	0.0003 (10)	-0.0025 (10)
C42	0.0361 (16)	0.0212 (13)	0.0211 (13)	0.0029 (12)	0.0047 (12)	-0.0023 (10)
C43	0.0319 (16)	0.0320 (15)	0.0198 (13)	0.0047 (12)	0.0014 (12)	-0.0045 (11)
C44	0.0260 (15)	0.0291 (15)	0.0286 (15)	0.0026 (12)	0.0001 (12)	-0.0103 (11)
C45	0.0379 (18)	0.0177 (14)	0.0469 (18)	-0.0007 (13)	0.0076 (15)	-0.0071 (12)
C46	0.0319 (16)	0.0226 (14)	0.0322 (15)	-0.0019 (12)	0.0103 (13)	-0.0006 (11)
C47	0.046 (2)	0.0356 (17)	0.0393 (18)	0.0028 (15)	0.0092 (16)	-0.0163 (13)

Geometric parameters (\AA , $^\circ$)

S1—C5	1.717 (3)	C41—C42	1.388 (4)
S1—C2	1.728 (2)	C41—C46	1.395 (4)
C2—N3	1.298 (3)	C42—C43	1.389 (4)
C2—N21	1.387 (3)	C42—H42	0.95
N3—C4	1.388 (3)	C43—C44	1.382 (4)
C4—C5	1.354 (3)	C43—H43	0.95
C4—C41	1.475 (3)	C44—C45	1.388 (4)
C5—H5	0.95	C44—C47	1.508 (4)
N21—C22	1.357 (3)	C45—C46	1.386 (4)
N21—H21	0.89 (3)	C45—H45	0.95
C22—O22	1.229 (3)	C46—H46	0.95
C22—C23	1.496 (3)	C47—H471	0.98
C23—H231	0.98	C47—H472	0.98
C23—H232	0.98	C47—H473	0.98
C23—H233	0.98		
C5—S1—C2	87.86 (12)	C42—C41—C4	120.3 (2)
N3—C2—N21	120.0 (2)	C46—C41—C4	121.6 (2)
N3—C2—S1	116.09 (18)	C43—C42—C41	121.2 (3)
N21—C2—S1	123.95 (18)	C43—C42—H42	119.4
C2—N3—C4	110.2 (2)	C41—C42—H42	119.4
C5—C4—N3	114.1 (2)	C44—C43—C42	121.1 (3)
C5—C4—C41	127.8 (2)	C44—C43—H43	119.5
N3—C4—C41	118.1 (2)	C42—C43—H43	119.5
C4—C5—S1	111.72 (19)	C43—C44—C45	117.6 (2)
C4—C5—H5	124.1	C43—C44—C47	121.0 (3)

S1—C5—H5	124.1	C45—C44—C47	121.4 (3)
C22—N21—C2	125.2 (2)	C46—C45—C44	122.0 (3)
C22—N21—H21	117.7 (18)	C46—C45—H45	119.0
C2—N21—H21	117.1 (18)	C44—C45—H45	119.0
O22—C22—N21	120.7 (2)	C45—C46—C41	120.1 (3)
O22—C22—C23	123.5 (2)	C45—C46—H46	119.9
N21—C22—C23	115.8 (2)	C41—C46—H46	119.9
C22—C23—H231	109.5	C44—C47—H471	109.5
C22—C23—H232	109.5	C44—C47—H472	109.5
H231—C23—H232	109.5	H471—C47—H472	109.5
C22—C23—H233	109.5	C44—C47—H473	109.5
H231—C23—H233	109.5	H471—C47—H473	109.5
H232—C23—H233	109.5	H472—C47—H473	109.5
C42—C41—C46	118.0 (2)		
C5—S1—C2—N3	0.0 (2)	N3—C4—C41—C42	-2.7 (4)
C5—S1—C2—N21	-179.6 (2)	C5—C4—C41—C46	-2.5 (4)
N21—C2—N3—C4	-180.0 (2)	N3—C4—C41—C46	177.9 (2)
S1—C2—N3—C4	0.4 (3)	C46—C41—C42—C43	0.2 (4)
C2—N3—C4—C5	-0.7 (3)	C4—C41—C42—C43	-179.3 (3)
C2—N3—C4—C41	179.0 (2)	C41—C42—C43—C44	0.3 (4)
N3—C4—C5—S1	0.7 (3)	C42—C43—C44—C45	-0.7 (4)
C41—C4—C5—S1	-179.0 (2)	C42—C43—C44—C47	179.4 (3)
C2—S1—C5—C4	-0.4 (2)	C43—C44—C45—C46	0.7 (5)
N3—C2—N21—C22	175.6 (2)	C47—C44—C45—C46	-179.4 (3)
S1—C2—N21—C22	-4.8 (4)	C44—C45—C46—C41	-0.2 (5)
C2—N21—C22—O22	1.1 (4)	C42—C41—C46—C45	-0.3 (4)
C2—N21—C22—C23	-178.5 (2)	C4—C41—C46—C45	179.2 (3)
C5—C4—C41—C42	177.0 (3)		

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N21—H21 \cdots O22 ⁱ	0.89 (3)	1.95 (3)	2.818 (3)	166 (3)

Symmetry code: (i) $x+1/2, -y+1/2, z-1/2$.**(II) 2-amino-4-tolyl-1,3-thiazolium chloride dihydrate***Crystal data*

$C_{10}H_{11}N_2S^+Cl^- \cdot 2H_2O$
 $M_r = 262.75$
 Orthorhombic, $P2_12_12_1$
 Hall symbol: P 2ac 2ab
 $a = 6.8815$ (6) \AA
 $b = 9.3072$ (14) \AA
 $c = 19.499$ (3) \AA
 $V = 1248.9$ (3) \AA^3
 $Z = 4$

$F(000) = 552$
 $D_x = 1.397$ Mg m^{-3}
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ \AA
 Cell parameters from 2244 reflections
 $\theta = 2.9\text{--}27.1^\circ$
 $\mu = 0.46$ mm^{-1}
 $T = 120$ K
 Needle, colourless
 $0.35 \times 0.02 \times 0.02$ mm

Data collection

Nonius KappaCCD area-detector
diffractometer
Radiation source: Bruker Nonius FR591
rotating anode
Graphite monochromator
Detector resolution: 9.091 pixels mm⁻¹
 φ and ω scans
9123 measured reflections

1441 independent reflections
1048 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.156$
 $\theta_{\text{max}} = 26.0^\circ$, $\theta_{\text{min}} = 3.0^\circ$
 $h = -8 \rightarrow 8$
 $k = -9 \rightarrow 11$
 $l = -23 \rightarrow 24$

Refinement

Refinement on F^2
Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.063$
 $wR(F^2) = 0.152$
 $S = 1.06$
1441 reflections
159 parameters
6 restraints
Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map
Hydrogen site location: inferred from
neighbouring sites
H atoms treated by a mixture of independent
and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0775P)^2 + 0.1085P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.44 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.47 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. Least-squares planes (x, y, z in crystal coordinates) and deviations from them (* indicates atom used to define plane)

6.8444 (0.0021) x + 0.9623 (0.0236) y - 0.1571 (0.0462) z = 4.5106 (0.0062)

* 0.0027 (0.0047) C41 * -0.0022 (0.0049) C42 * 0.0001 (0.0049) C43 * 0.0015 (0.0043) C44 * -0.0010 (0.0047) C45 *
-0.0011 (0.0050) C46

Rms deviation of fitted atoms = 0.0016

6.8599 (0.0018) x - 0.7208 (0.0273) y - 0.3258 (0.0468) z = 4.2195 (0.0099)

Angle to previous plane (with approximate e.s.d.) = 10.39 (0.07)

* -0.0004 (0.0030) S1 * -0.0028 (0.0037) C2 * 0.0053 (0.0042) N3 * -0.0057 (0.0043) C4 * 0.0035 (0.0038) C5

Rms deviation of fitted atoms = 0.0040

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.6173 (2)	0.10019 (18)	-0.17494 (9)	0.0381 (5)
N3	0.6432 (7)	0.2996 (5)	-0.0877 (3)	0.0312 (12)
H3	0.6547	0.3855	-0.0693	0.039*
N21	0.6430 (7)	0.3850 (6)	-0.2005 (3)	0.0354 (12)
H21	0.6521	0.4742	-0.1860	0.044*
H22	0.6383	0.3667	-0.2447	0.044*
C2	0.6365 (9)	0.2782 (7)	-0.1558 (3)	0.0339 (15)
C4	0.6302 (9)	0.1739 (6)	-0.0486 (3)	0.0295 (14)
C5	0.6176 (10)	0.0580 (7)	-0.0872 (3)	0.0398 (16)
H5	0.6096	-0.0370	-0.0696	0.050*
C41	0.6339 (9)	0.1855 (7)	0.0270 (3)	0.0309 (14)
C42	0.6516 (9)	0.0617 (7)	0.0679 (3)	0.0349 (15)
H42	0.6633	-0.0302	0.0471	0.044*
C43	0.6518 (9)	0.0744 (7)	0.1385 (3)	0.0355 (16)

H43	0.6643	-0.0097	0.1658	0.044*
C44	0.6342 (9)	0.2060 (7)	0.1704 (4)	0.0347 (14)
C45	0.6158 (9)	0.3280 (7)	0.1304 (3)	0.0327 (15)
H45	0.6031	0.4197	0.1514	0.041*
C46	0.6158 (9)	0.3156 (7)	0.0592 (3)	0.0335 (15)
H46	0.6030	0.3999	0.0321	0.042*
C47	0.6348 (10)	0.2194 (7)	0.2479 (3)	0.0392 (16)
H471	0.5830	0.1311	0.2683	0.049*
H472	0.5537	0.3011	0.2616	0.049*
H473	0.7682	0.2347	0.2640	0.049*
Cl1	0.6618 (2)	0.63450 (17)	-0.07781 (8)	0.0390 (5)
O1W	0.3448 (7)	0.7854 (6)	-0.1681 (2)	0.0447 (12)
H11W	0.432 (7)	0.741 (8)	-0.143 (3)	0.056*
H12W	0.240 (6)	0.787 (8)	-0.142 (3)	0.056*
O2W	0.5451 (7)	0.6804 (5)	0.0803 (3)	0.0437 (12)
H21W	0.447 (7)	0.739 (6)	0.086 (3)	0.055*
H22W	0.556 (10)	0.669 (8)	0.0358 (12)	0.055*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0377 (9)	0.0418 (9)	0.0347 (9)	0.0028 (8)	-0.0041 (8)	-0.0082 (8)
N3	0.029 (3)	0.040 (3)	0.024 (3)	0.002 (2)	-0.002 (2)	-0.003 (2)
N21	0.037 (3)	0.042 (3)	0.027 (3)	-0.002 (3)	-0.002 (2)	-0.003 (2)
C2	0.028 (3)	0.046 (4)	0.027 (4)	-0.002 (3)	0.001 (3)	-0.009 (3)
C4	0.033 (3)	0.027 (3)	0.028 (3)	0.003 (3)	-0.004 (3)	0.000 (3)
C5	0.041 (4)	0.043 (4)	0.036 (4)	0.005 (3)	-0.002 (3)	0.006 (3)
C41	0.030 (3)	0.035 (4)	0.027 (3)	0.000 (3)	-0.001 (3)	0.000 (3)
C42	0.037 (4)	0.036 (4)	0.031 (4)	0.003 (3)	-0.005 (3)	-0.005 (3)
C43	0.030 (3)	0.037 (4)	0.039 (4)	0.004 (3)	0.004 (3)	0.010 (3)
C44	0.026 (3)	0.049 (4)	0.030 (3)	-0.001 (3)	0.002 (3)	0.004 (3)
C45	0.032 (3)	0.036 (4)	0.029 (3)	0.001 (3)	0.004 (3)	-0.007 (3)
C46	0.036 (4)	0.037 (4)	0.028 (3)	0.005 (3)	-0.003 (3)	0.006 (3)
C47	0.039 (4)	0.051 (4)	0.028 (4)	-0.002 (4)	0.008 (3)	0.005 (3)
Cl1	0.0406 (9)	0.0407 (9)	0.0357 (9)	-0.0016 (7)	-0.0011 (8)	0.0008 (8)
O1W	0.046 (3)	0.062 (3)	0.026 (3)	0.000 (3)	0.000 (2)	0.008 (2)
O2W	0.045 (3)	0.054 (3)	0.032 (3)	0.009 (2)	-0.002 (2)	-0.007 (3)

Geometric parameters (Å, °)

S1—C2	1.704 (7)	C43—C44	1.379 (9)
S1—C5	1.755 (7)	C43—H43	0.95
N3—C2	1.342 (8)	C44—C45	1.383 (9)
N3—C4	1.400 (8)	C44—C47	1.516 (9)
N3—H3	0.88	C45—C46	1.395 (9)
N21—C2	1.322 (8)	C45—H45	0.95
N21—H21	0.88	C46—H46	0.95
N21—H22	0.88	C47—H471	0.98

C4—C5	1.318 (9)	C47—H472	0.98
C4—C41	1.479 (9)	C47—H473	0.98
C5—H5	0.95	O1W—H11W	0.88 (6)
C41—C46	1.369 (9)	O1W—H12W	0.88 (5)
C41—C42	1.407 (9)	O2W—H21W	0.88 (5)
C42—C43	1.382 (9)	O2W—H22W	0.88 (2)
C42—H42	0.95		
C2—S1—C5	90.2 (3)	C41—C42—H42	120.2
C2—N3—C4	114.4 (5)	C42—C43—C44	121.7 (6)
C2—N3—H3	122.8	C42—C43—H43	119.2
C4—N3—H3	122.8	C44—C43—H43	119.2
C2—N21—H21	120.0	C43—C44—C45	118.9 (6)
C2—N21—H22	120.0	C43—C44—C47	121.5 (6)
H21—N21—H22	120.0	C45—C44—C47	119.6 (6)
N21—C2—N3	122.6 (6)	C44—C45—C46	119.6 (6)
N21—C2—S1	126.1 (5)	C44—C45—H45	120.2
N3—C2—S1	111.3 (5)	C46—C45—H45	120.2
C5—C4—N3	112.1 (5)	C41—C46—C45	121.9 (6)
C5—C4—C41	129.1 (6)	C41—C46—H46	119.0
N3—C4—C41	118.8 (5)	C45—C46—H46	119.0
C4—C5—S1	111.9 (5)	C44—C47—H471	109.5
C4—C5—H5	124.0	C44—C47—H472	109.5
S1—C5—H5	124.0	H471—C47—H472	109.5
C46—C41—C42	118.2 (6)	C44—C47—H473	109.5
C46—C41—C4	121.3 (6)	H471—C47—H473	109.5
C42—C41—C4	120.4 (5)	H472—C47—H473	109.5
C43—C42—C41	119.6 (6)	H11W—O1W—H12W	104 (3)
C43—C42—H42	120.2	H21W—O2W—H22W	105 (3)
C4—N3—C2—N21	178.7 (6)	N3—C4—C41—C42	-170.1 (6)
C4—N3—C2—S1	-0.9 (8)	C46—C41—C42—C43	-0.5 (10)
C5—S1—C2—N21	-179.2 (7)	C4—C41—C42—C43	-179.0 (6)
C5—S1—C2—N3	0.3 (5)	C41—C42—C43—C44	0.3 (11)
C2—N3—C4—C5	1.2 (9)	C42—C43—C44—C45	0.1 (10)
C2—N3—C4—C41	-179.3 (6)	C42—C43—C44—C47	-179.9 (6)
N3—C4—C5—S1	-1.0 (8)	C43—C44—C45—C46	-0.2 (10)
C41—C4—C5—S1	179.6 (6)	C47—C44—C45—C46	179.8 (6)
C2—S1—C5—C4	0.4 (6)	C42—C41—C46—C45	0.4 (10)
C5—C4—C41—C46	-169.2 (7)	C4—C41—C46—C45	178.9 (6)
N3—C4—C41—C46	11.4 (10)	C44—C45—C46—C41	-0.1 (11)
C5—C4—C41—C42	9.2 (12)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N3—H3...C11	0.88	2.32	3.126 (5)	151
N21—H21...C11	0.88	2.58	3.337 (6)	144

N21—H22...O1W ⁱ	0.88	1.86	2.726 (7)	166
O1W—H11W...C11	0.88 (6)	2.26 (6)	3.136 (5)	178 (7)
O1W—H12W...O2W ⁱⁱ	0.88 (5)	1.83 (3)	2.700 (7)	169 (8)
O2W—H22W...C11	0.88 (2)	2.35 (2)	3.214 (5)	167 (6)
O2W—H21W...C11 ⁱⁱ	0.88 (5)	2.29 (3)	3.151 (5)	166 (6)

Symmetry codes: (i) $-x+1, y-1/2, -z-1/2$; (ii) $x-1/2, -y+3/2, -z$.