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2-Ammonio-5-chloro-4-methylbenzenesulfonate, its 1-methyl-2-pyrrolidone and dimethyl sulfoxide monosolvates and a corrected structure of 2,2′-(1,4-phenylene)-di(4,5-dihydroimidazolium) bis(4-aminobenzenesulfonate) dihydrate

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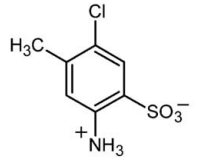
2-Ammonio-5-chloro-4-methylbenzenesulfonate, $C_7H_8ClNO_3S$, (I*a*), is an intermediate in the synthesis of lake red azo pigments. The present structure determination from single-crystal data confirms the results of a previous powder diffraction determination [Bekö, Thoms, Brüning, Alig, van de Streek, Lakatos, Glaubitz & Schmidt (2010). *Z. Kristallogr.* **225**, 382–387]. The zwitterionic tautomeric form is confirmed. During a polymorph screening, two additional pseudopolymorphs were obtained, *viz.* 2-ammonio-5-chloro-4-methylbenzenesulfonate 1-methyl-2-pyrrolidone monosolvate, $C_7H_8ClNO_3S\cdot C_5H_9NO$, (I*b*), and 2-ammonio-5-chloro-4-methylbenzenesulfonate dimethyl sulfoxide monosolvate, $C_7H_8ClNO_3S\cdot C_2H_6OS$, (I*c*). The molecules of (I*b*) have crystallographic *m* symmetry. The 1-methyl-2-pyrrolidone solvent molecule has an envelope conformation and is disordered around the mirror plane. The structure shows hydrogen-bonded ladders of molecules [graph-set notation $C_2^2(6)R_2^2(12)$] in the [010] direction. The benzene groups of adjacent ladders are also stacked in this direction. A different type of hydrogen-bonded ladder [graph-set notation $C(6)R_2^2(4)R_4^4(12)$] occurs in (I*c*). In (I*a*), (I*b*) and (I*c*), the molecules correspond to the zwitterionic tautomer. The structure of the cocrystal of 4-aminobenzenesulfonic acid with 1,4-bis(4,5-dihydroimidazol-2-yl)benzene [Shang, Ren, Wang, Lu & Yang (2009). *Acta Cryst.* E**65**, o2221–o2222] is corrected; it actually contains 4-aminobenzenesulfonate anions and 2,2′-(1,4-phenylene)di(dihydroimidazolium) dications, *i.e.* 2,2′-(1,4-phenylene)di(4,5-dihydroimidazolium) bis(4-aminobenzenesulfonate) dihydrate, $C_{12}H_{16}N_4^{2+}\cdot 2C_6H_6NO_3S^-\cdot 2H_2O$. Hence, all known structures of aminobenzenesulfonic acid complexes contain ionic or zwitterionic molecules; there is no known structure with a neutral aminobenzenesulfonic acid molecule.

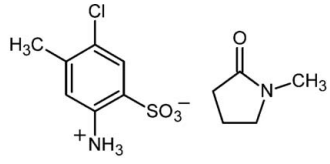
Comment

2-Ammonio-5-chloro-4-methylbenzenesulfonate, (I*a*), also called CLT acid (from **ch**loro-amino-**t**oluenesulfonic acid), is industrially produced on the scale of several tens of thousands of tonnes per year. It is used as an intermediate in the synthesis of lake red azo pigments (*e.g.* Pigment Red 52:1, 52:2, 53, 53:1, 53:2, 53:3) for newspapers and journals. It can exist in two possible tautomers, *viz.* as a non-zwitterion (2-amino-5-chloro-4-methylbenzenesulfonic acid), having an $-NH_2$ and an $-SO_3H$ group, and as a zwitterion (2-ammonio-5-chloro-4-methylbenzenesulfonate), with $-NH_3^+$ and $-SO_3^-$ groups. A crystal structure of the compound was determined by Bekö *et al.* (2010) from powder diffraction data, as no suitable single crystals were available at that time. The powder data clearly showed that the compound exists as the zwitterionic tautomer.

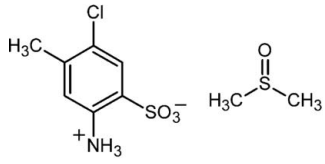
Polymorph screening of (I*a*) was performed by crystallizing the compound from a variety of solvents and using various methods of crystallization. The polymorph screening resulted in single crystals suitable for X-ray diffraction of the solvent-free compound (I*a*), its 1-methyl-2-pyrrolidone (NMP) monosolvate, (I*b*), and its dimethyl sulfoxide (DMSO) monosolvate, (I*c*). Other polymorphs, pseudopolymorphs or hydrates could not be found.



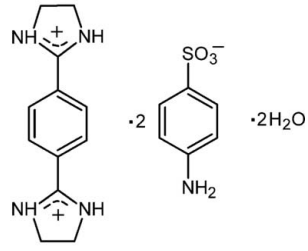
(I*a*)



(I*b*)



(I*c*)



(II)

The molecular structure of (I*a*) is shown in Fig. 1. The result of the previous powder diffraction determination (Bekö *et al.*, 2010) and the tautomeric form are confirmed, but the hydrogen-bonding system (Table 1) is more accurately derived from the present single-crystal determination. The molecules are connected by N—H···O hydrogen bonds to form double layers parallel to (010). A weak intermolecular C—H···O contact also adds to the stabilization within the layer. Adjacent double layers are connected by a very weak intermolecular C_{methyl}—H···Cl contact with an H···Cl distance of 3.02 Å. For a further description of the structure, see Bekö *et al.* (2010).

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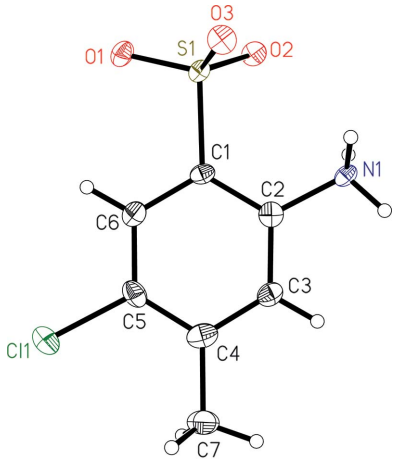

Figure 1
The molecular structure of (I*a*), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

Compound (I*b*) crystallizes in the monoclinic space group $P2_1/m$ with the 2-ammonio-5-chloro-4-methylbenzenesulfonate molecule positioned on a crystallographic mirror plane. The NMP solvent molecule is disordered about the crystallographic mirror plane and has a C10-envelope conformation. The molecular structure and numbering scheme are shown in Fig. 2 and the crystal packing is shown in Fig. 3. The 2-amino-5-chloro-4-methyl-benzenesulfonate molecules are connected by two intermolecular N—H···O hydrogen bonds between the $-NH_3^+$ and $-SO_3^-$ groups (Table 2) to form a ladder structure in the [010] direction (Fig. 4). In graph-set notation (Etter *et al.*, 1990; Bernstein *et al.*, 1995), the hydrogen-bond pattern of the ladder structure is $C_2^2(6)R_2^2(12)$. The third H atom of the $-NH_3^+$ group forms an N—H···O hydrogen bond with the NMP molecule. The benzene groups of adjacent ladders form stacks along [010]. The interplanar distance in the stack is $b/2$ = 3.473 (3) Å, which is a suitable distance for π–π contacts between the benzene groups. Hence the ladders, running in the *b*-axis direction, are locked together with neighbouring ladders along the *a*-axis direction, resulting in a two-dimensional framework parallel to the (001) plane.

The DMSO solvate, (I*c*), crystallizes in the triclinic space group $P\overline{1}$. The asymmetric unit contains one 2-ammonio-5-chloro-4-methylbenzenesulfonate molecule and one DMSO molecule. The molecular structure and numbering scheme are shown in Fig. 5 and the crystal packing is shown in Fig. 6. The

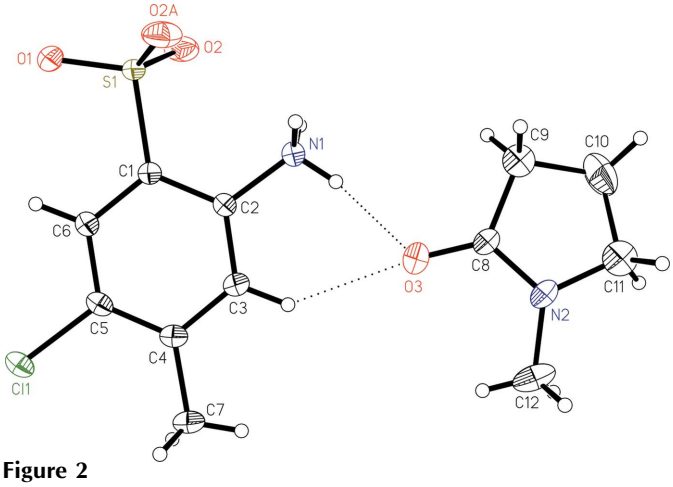

Figure 2
The molecular structure of (I*b*), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. The second possible position of the disordered 1-methyl-2-pyrrolidone molecule has been omitted. Dotted lines indicate hydrogen bonds. [Symmetry code: (A) $x, -y+\frac{1}{2}, z$.]

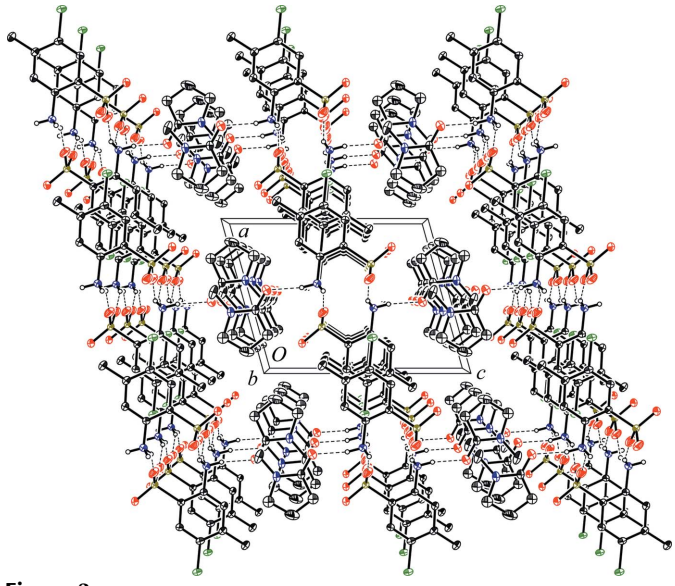

Figure 3
The crystal packing of (I*b*), viewed down [010]. Hydrogen bonds are shown as dashed lines and C-bound H atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level.

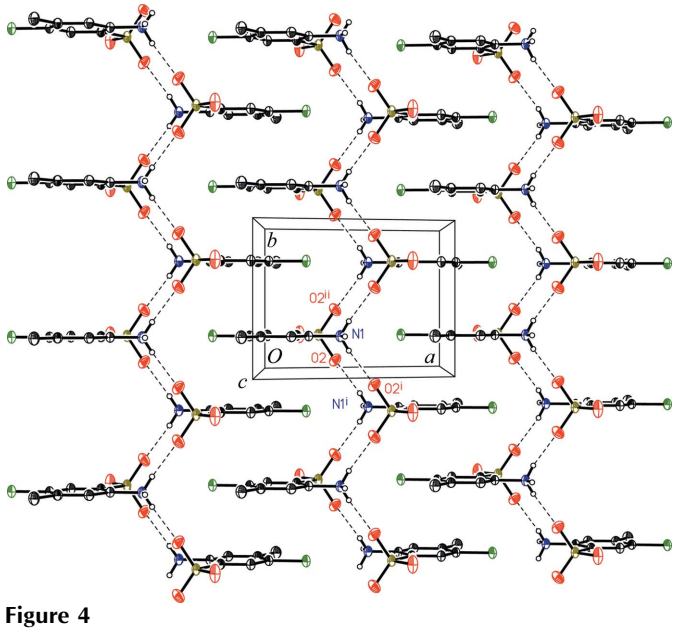

Figure 4
A section of the structure of (I*b*), showing the hydrogen-bonded ladders and the stacking of the benzene groups; the view direction is [001]. Hydrogen bonds are shown as dashed lines and C-bound H atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $-x+1, -y, -z+1$; (ii) $x, -y+\frac{1}{2}, z$.]

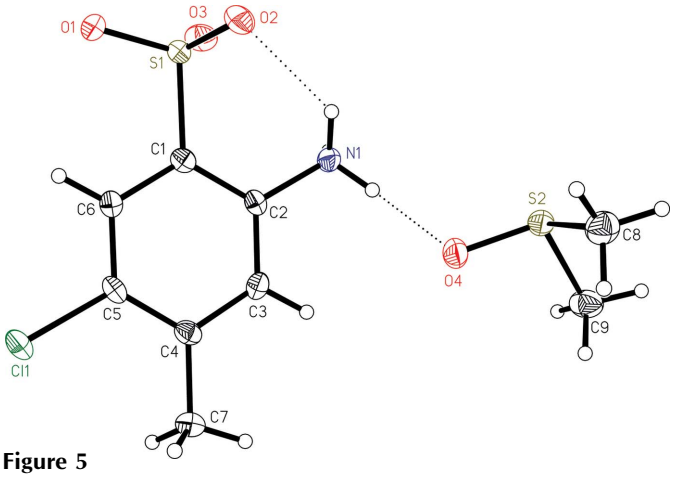

Figure 5
The molecular structure of (I*c*), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. Dotted lines indicate hydrogen bonds.

molecules are arranged by hydrogen bonding (Table 3) to form a ladder structure parallel to the *a*-axis direction. A detailed view of the ladder structure is shown in Fig. 7. Each 2-ammonio-5-chloro-4-methylbenzenesulfonate molecule is connected by four N—H···O hydrogen bonds to three neighbouring molecules. The N1—H1*B* bond is bifurcated and has longer H···O contact distances than the remaining hydrogen bonds. In terms of graph-set analysis, the hydrogen-bond pattern of the ladder structure is $C(6)R_4^4(12)$. Here, $C(6)$ represents the repetition of the structure along the *a*-axis direction by the N1—H1*C*···O1^{ii} hydrogen bond [symmetry code: (ii) $x+1, y, z$], while the ring structure results from the combination of N1—H1*C*···O1^{ii} and N1—H1*B*···O2^{i} hydrogen bonds and an inversion centre [symmetry code: (i) $-x+1, -y+1, -z+1$]. The bifurcated N1—H1*B* bond, which is involved in both an intra- and an intermolecular hydrogen bond, results in an additional four-membered ring [graph-set notation $R_2^2(4)$]. The DMSO solvent molecule is attached to the ladder by an additional N—H···O hydrogen bond and by a very weak intermolecular DMSO–sulfonate C—H···O

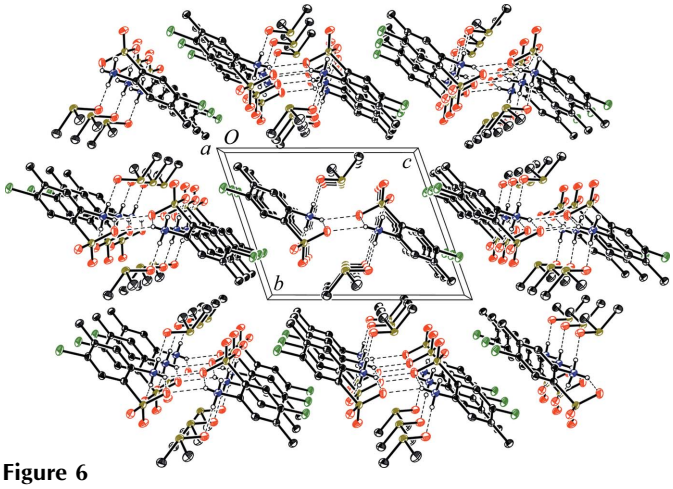

Figure 6
The crystal packing of (I*c*), viewed down [100]. Hydrogen bonds are shown as dashed lines and C-bound H atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level.

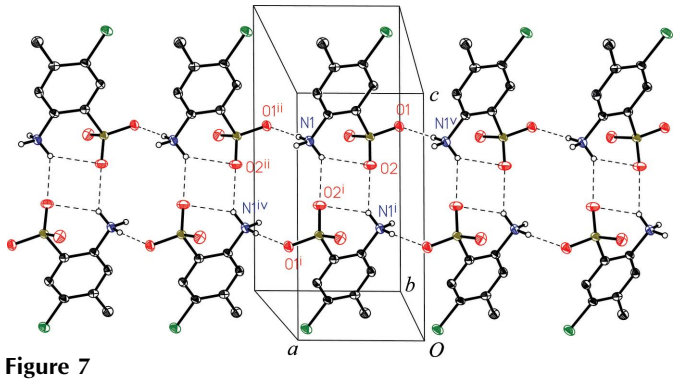

Figure 7
A view of the ladder structure of (I*c*). Hydrogen bonds are shown as dashed lines and C-bound H atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $x+1, y, z$; (iv) $-x+2, -y+1, -z+1$; (v) $x-1, y, z$.]

interaction (Table 3). Adjacent ladders are connected by a weak intermolecular DMSO–DMSO C—H···O interaction. The ladders form a hexagonal rod packing.

In all three structures, the main molecule exists as a 2-ammoniobenzenesulfonate zwitterion rather than as 2-aminobenzenesulfonic acid. A search of the Cambridge Structural Database (Version 5.32, with August 2011 update; Allen, 2002) for compounds containing 2-, 3- and 4-aminobenzenesulfonic acid revealed 29 entries with a zwitterionic molecule. Only the structure of Shang *et al.* (2009) is reported to contain a neutral molecule. Surprisingly, the three S—O bond distances in that determination are almost equal, which is rather suspicious for a sulfonic acid. Therefore, we decided to redetermine that structure from the published reflection data. The results are presented here as structure (II). As expected, the assignment of the sulfonic acid H atom turned out to be incorrect. Also, one of the H-atom positions on the water molecule had to be modified. The revised structure contains 4-aminobenzenesulfonate anions and 1,4-bis(4,5-dihydroimidazol-2-yl)benzene dications, rather than neutral molecules. Thus, all reported crystal structures of aminobenzenesulfonic acids contain zwitterionic molecules or ions. There is no known structure with a neutral aminobenzenesulfonic acid molecule. The corrected hydrogen bonds of structure (II) are given in Table 4. A view of the structure is shown in Fig. 8. For a discussion of the structure, see Shang *et al.* (2009).

In the structures reported here, all H atoms of the ammonio groups are donors of N—H···O hydrogen bonds. In (I*a*), which does not contain solvent molecules, all three H atoms are connected to sulfonate O atoms of neighbouring molecules, resulting in a two-dimensional framework. In both (I*b*) and (I*c*), one N—H bond donates a hydrogen bond to a solvent O atom. Thus, only two H atoms are left for hydrogen-bond formation with sulfonate O atoms. In both cases, this results in ladder-type structures, but they are rather different: in (I*b*), each molecule in the ladder is connected to only two neighbouring molecules, resulting in $R_2^2(12)$ rings, while in (I*c*), each molecule is connected to three neighbouring molecules, resulting in $R_2^2(4)$ and $R_4^4(12)$ rings.

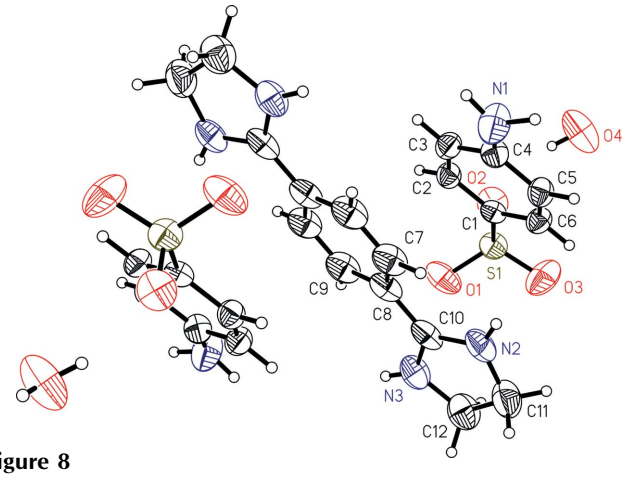

Figure 8
The revised molecular structure of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. Unlabelled atoms are related to labelled atoms by an inversion centre at the mid-point of the central six-membered ring.

Experimental

The polymorph screening of (I*a*) was carried out using commercially available 2-ammonio-5-chloro-4-methylbenzenesulfonate, obtained from abcr GmbH and Co. KG, Germany (purity >98%). For purification, the starting material was recrystallized twice from boiling water. Compound (I*a*) was found to be soluble at room temperature in quinoline, morpholine, 2-picoline, *N*,*N*′-dimethylformamide, *N*,*N*′-dimethylacetamide, 1-methyl-2-pyrrolidone (NMP) and dimethyl sulfoxide (DMSO). Subsequently, different methods of crystallization were employed, including: (i) slurry experiments by suspending (I*a*) in different solvents at room temperature; (ii) evaporation crystallization at room temperature and at 353 K; (iii) slow or rapid antisolvent crystallization by overlaying a solution of (I*a*) with an antisolvent; (iv) heating under reflux with subsequent slow or fast cooling; (v) treatment of a solution or a suspension of (I*a*) in an ultrasonic bath at room temperature; (vi) slow or rapid vapour diffusion experiments by diffusion of an antisolvent into a solution of (I*a*) *via* the gas phase. A multitude of different organic solvents were used as antisolvents, *e.g.* ketones, ethers, esters, alcohols, benzene, benzene derivatives (*e.g.* toluene, picolines and chlorobenzenes) and alkanes, and water. All solids thus obtained were analysed using X-ray powder diffraction data recorded under ambient conditions in transmission mode on a Stoe STADI-P diffractometer with a Ge(111) monochromator and a linear position-sensitive detector using Cu $K\alpha_1$ radiation (λ = 1.5406 Å).

IR spectra were measured on an FT–IR-8300 device (Shimadzu). The samples were prepared as KBr pellets, with 300 mg KBr to 2 mg of sample. ^{1}H NMR spectra were measured on a Bruker Avance 300 device at 300 MHz in tubes filled with d_6-DMSO and about 5 mg of substance. Elemental analyses (CHNS) were carried out on an Elementar (vario MICRO cube) elemental analyser; about 1 to 4 mg of each sample was placed in a tin vessel and measured at 1423 K under a helium atmosphere with addition of oxygen during the measurement.

Colourless single crystals of (I*a*) were obtained by dissolving the purified starting material (400 mg) in 1-methyl-2-pyrrolidone (30 ml) under reflux and then filtering the hot solution. The solution was left for evaporation crystallization at room temperature for 54 weeks. Upon reduction of the supernatant to 5 ml, colourless single crystals of (I*a*) had formed. The precipitate was isolated by filtration, washed with acetone and dried at room temperature. IR (KBr, ν, cm^{-1}): 3091 (*m*), 3039 (*m*), 2854 (*m*), 2613 (*m*), 1757 (*w*), 1560 (*s*), 1477 (*m*), 1375 (*m*), 1230 (*s*), 1195 (*s*), 1116 (*s*), 1043 (*s*), 739 (*m*), 719 (*m*), 636 (*s*); ^{1}H NMR (300 MHz, d_6-DMSO): δ 7.57 (*s*, 1H, Ar—H), 7.05 (*s*, 1H, Ar—H), 6.9–6.0 [*s* (broad), 3H, Ar—NH_3^+], 2.29 (s, 3H, Ar—CH_3); elemental analysis calculated for $C_7H_8ClNO_3S$ (%): C 37.93, H 3.64, N 6.32, S 14.47; found: C 37.67, H 3.58, N 6.16, S 14.68.

Suitable single crystals of (I*b*) were obtained by treatment of the purified starting material (20 mg) with 1-methyl-2-pyrrolidone (3 ml) in an ultrasonic bath at room temperature for 30 min. After 2 d, colourless plate-shaped crystals of (I*b*) were obtained. The precipitate was isolated by filtration and dried for one day at room temperature. IR (KBr, ν, cm^{-1}): 3101 (*m*), 3040 (*m*), 3017 (*m*), 2961 (*m*), 2926 (*m*), 2855 (*m*), 2833 (*m*), 2613 (*s*), 1773 (*m*), 1757 (*m*), 1734 (*m*), 1684 (*s*), 1653 (*s*), 1633 (*m*), 1591 (*m*), 1576 (*s*), 1560 (*s*), 1541 (*s*), 1522 (*s*), 1508 (*s*), 1477 (*s*), 1437 (*m*), 1375 (*s*), 1288 (*m*), 1230 (*s*), 1196 (*s*), 1165 (*s*), 1117 (*s*), 1080 (*m*), 1043 (*s*), 739 (*s*), 719 (*s*), 636 (*s*), 567 (*s*); ^{1}H NMR (300 MHz, d_6-DMSO): δ 7.57 (*s*, 1H, Ar—H), 7.04 (*s*, 1H, Ar—H), 5.00–3.50 [*s* (broad), 3H, Ar—NH_3^+], 3.32–3.27 [*m*, 2H, CH_2 (NMP)], 2.69 [*s*, 3H, CH_3 (NMP)], 2.28 (*s*, 3H, Ar—CH_3), 2.19–2.15 [*m*, 2H, CH_2 (NMP)], 1.95–1.84 [*m*, 2H, CH_2 (NMP)]; elemental analysis calculated for $C_7H_8ClNO_3S{\cdot}C_5H_9NO$ (%): C 44.93, H 5.34, N 8.73, S 10.00; found: C 44.72, H 5.31, N 8.62, S 10.20.

Suitable single crystals of (I*c*) were obtained by treatment of the purified starting material (500 mg) with dimethyl sulfoxide (3 ml) in an ultrasonic bath at room temperature for 30 min. After 3 d, colourless block-shaped crystals of (I*c*) were obtained. The precipitate was isolated by filtration and dried for 1 d at room temperature. IR (KBr, ν, cm^{-1}): 3121 (*m*), 3086 (*m*), 3063 (*m*), 3007 (*m*), 2920 (*m*), 2853 (*m*), 2627 (*m*), 1593 (*m*), 1558 (*s*), 1549 (*s*), 1506 (*s*), 1373 (*s*), 1308 (*m*), 1290 (*m*), 1238 (*s*), 1204 (*s*), 1165 (*s*), 1117 (*s*), 1078 (*s*), 1038 (*s*), 1003 (*s*), 735(*s*), 721 (*s*), 710 (*m*), 637 (*s*), 563 (*s*); ^{1}H NMR (300 MHz, d_6-DMSO): δ 7.56 (*s*, 1H, Ar—H), 7.03 (*s*, 1H, Ar—H), 5.50–3.50 [*s* (broad), 3H, Ar—NH_3^+], 2.54 (*s*, 6H, DMSO), 2.28 (*s*, 3H, Ar—CH_3); elemental analysis calculated for $C_7H_8ClNO_3S{\cdot}C_2H_6OS$ (%): C 36.06, H 4.71, N 4.67, S 21.39; found: C 35.90, H 4.72, N 4.52, S 21.56.

Compound (I*a*)

Crystal data

$C_7H_8ClNO_3S$
M_r = 221.65
Monoclinic, *Ia*
a = 4.9308 (3) Å
b = 32.364 (2) Å
c = 5.4922 (4) Å
β = 93.654 (1)°
V = 874.68 (10) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.65 mm^{-1}
T = 173 K
0.40 × 0.20 × 0.06 mm

Data collection

Siemens SMART 1K CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2000)
T_{min} = 0.693, T_{max} = 0.962
5429 measured reflections
2101 independent reflections
1934 reflections with $I > 2\sigma(I)$
R_{int} = 0.038

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.093
S = 1.05
2101 reflections
131 parameters
2 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.68 e Å^{-3}
$\Delta\rho_{min}$ = −0.51 e Å^{-3}
Absolute structure: Flack (1983), with 986 Friedel pairs
Flack parameter: 0.04 (8)

Table 1
Hydrogen-bond geometry (Å, °) for (I*a*).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···O3^{i}	0.91 (4)	1.88 (4)	2.772 (4)	166 (4)
N1—H1B···O1^{ii}	0.84 (4)	2.05 (4)	2.831 (4)	156 (3)
N1—H1C···O2^{iii}	0.93 (4)	1.95 (4)	2.809 (3)	155 (3)
C3—H3A···O1^{ii}	0.95	2.37	3.148 (3)	138
C7—H7C···Cl1^{iv}	0.98	3.02	3.925 (3)	154

Symmetry codes: (i) $x-1, y, z$; (ii) $x-1, y, z-1$; (iii) $x, -y+\frac{3}{2}, z-\frac{1}{2}$; (iv) $x-\frac{1}{2}, -y+1, z$.

Table 2
Hydrogen-bond geometry (Å, °) for (I*b*).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···O2^{i}	0.86 (2)	1.98 (2)	2.785 (2)	156 (2)
N1—H1B···O3	0.86 (3)	1.90 (3)	2.750 (2)	169 (3)
C3—H3A···O3	0.95	2.33	3.112 (3)	139

Symmetry code: (i) $-x+1, -y, -z+1$.

Compound (I*b*)

Crystal data

$C_7H_8ClNO_3S\cdot C_5H_9NO$
M_r = 320.79
Monoclinic, $P2_1/m$
a = 9.1917 (17) Å
b = 6.9457 (11) Å
c = 11.8265 (13) Å
β = 105.538 (7)°
V = 727.44 (19) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.42 mm^{-1}
T = 165 K
0.40 × 0.36 × 0.10 mm

Data collection

Siemens SMART 1K CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2000)
T_{min} = 0.889, T_{max} = 0.959
12236 measured reflections
2552 independent reflections
2131 reflections with $I > 2\sigma(I)$
R_{int} = 0.028

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.101
S = 1.01
2552 reflections
139 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.56 e Å^{-3}
$\Delta\rho_{min}$ = −0.57 e Å^{-3}

Compound (I*c*)

Crystal data

$C_7H_8ClNO_3S\cdot C_2H_6OS$
M_r = 299.78
Triclinic, $P\overline{1}$
a = 6.0394 (12) Å
b = 9.4441 (14) Å
c = 11.8044 (16) Å
α = 71.078 (11)°
β = 89.466 (16)°
γ = 81.207 (17)°
V = 628.83 (18) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.64 mm^{-1}
T = 167 K
0.40 × 0.30 × 0.20 mm

Data collection

Siemens SMART 1K CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2000)
T_{min} = 0.779, T_{max} = 0.880
10341 measured reflections
3481 independent reflections
2398 reflections with $I > 2\sigma(I)$
R_{int} = 0.057

Table 3
Hydrogen-bond geometry (Å, °) for (I*c*).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···O4	0.96 (3)	1.74 (3)	2.695 (2)	173 (2)
N1—H1B···O2	0.93 (2)	2.31 (2)	3.013 (2)	132 (2)
N1—H1B···O2^{i}	0.93 (2)	2.10 (2)	2.883 (2)	141 (2)
N1—H1C···O1^{ii}	0.82 (3)	2.02 (3)	2.818 (2)	162 (3)
C9—H9B···O4^{iii}	0.98	2.40	3.356 (3)	166
C9—H9C···O3^{iv}	0.98	2.50	3.231 (3)	131

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

Table 4
Hydrogen-bond geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···O3^{i}	1.00 (3)	1.97 (3)	2.949 (3)	167 (2)
N1—H1B···O1^{ii}	0.87 (3)	2.40 (3)	3.174 (3)	149 (2)
N1—H1B···O2^{ii}	0.87 (3)	2.48 (3)	3.214 (3)	143 (2)
N2—H2B···O4^{iii}	0.78 (3)	2.04 (3)	2.756 (3)	152 (2)
N3—H3B···O2^{iv}	0.79 (2)	2.12 (2)	2.894 (3)	169 (2)
O4—H4A···O2	0.81 (2)	2.04 (2)	2.822 (3)	161 (2)
O4—H4B···O1^{v}	0.80 (3)	2.02 (3)	2.816 (3)	172 (3)

Symmetry codes: (i) $x, -y+\frac{1}{2}, z-\frac{1}{2}$; (ii) $-x+\frac{1}{2}, -y, z-\frac{1}{2}$; (iii) $x-\frac{1}{2}, -y+\frac{1}{2}, -z+1$; (iv) $x-\frac{1}{2}, y, -z+\frac{3}{2}$; (v) $x+\frac{1}{2}, y, -z+\frac{3}{2}$.

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.081
S = 0.98
3481 reflections
169 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.42 e Å^{-3}
$\Delta\rho_{min}$ = −0.38 e Å^{-3}

Compound (II)

Crystal data and *Data collection*

See Shang *et al.* (2009)

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.065
S = 0.87
2346 reflections
205 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.20 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}

Compound (I*a*) was refined in the nonstandard space group *Ia*, rather than in *Cc*, in order to avoid a very large monoclinic angle of β = 129.887 (1)°. N- and O-bound H atoms were taken from difference Fourier syntheses and refined. C-bound H atoms were positioned geometrically and treated as riding, with aromatic C—H = 0.95 Å, methyl C—H = 0.98 Å and methylene C—H = 0.99 Å, and U_{iso}(H) = 1.2U_{eq}(non-methyl C) or 1.5U_{eq}(methyl C) for (I*a*), (I*b*) and (I*c*), and with aromatic C—H = 0.93 Å and methylene C—H = 0.97 Å, and U_{iso}(H) = 1.2U_{eq}(C) for (II). The H atoms on atoms C7 and C12 of (I*b*) were taken from a difference synthesis and refined. The pyrrolidone ring atoms C9, C10 and C11 of (I*b*) were found to be displaced from the mirror plane and so they are disordered and were refined with site-occupation factors of 0.5.

Data collection: *SMART* (Siemens, 1995) for (I*a*), (I*b*) and (I*c*); *SMART* (Bruker, 1998) for (II). Cell refinement: *SAINT* (Siemens, 1995) for (I*a*); *SMART* (Siemens, 1995) for (I*b*) and (I*c*); *SAINT* (Bruker, 1998) for (II). Data reduction: *SAINT* (Siemens, 1995) for (I*a*), (I*b*) and (I*c*); *SAINT* (Bruker, 1998) for (II). For all compounds, program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3426). Services for accessing these data are described at the back of the journal.

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