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The anilinium chloride adduct of 4-bromo-*N*-phenylbenzenesulfonamide

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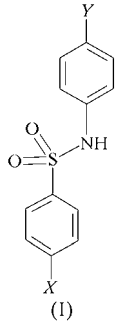
The title compound anilinium chloride–4-bromo-*N*-phenylbenzenesulfonamide (1/1), $C_6H_8N^+\cdot Cl^-\cdot C_{12}H_{10}BrNO_2S$, displays a hydrogen-bonded ladder motif with four independent N—H···Cl bonds in which both the NH group of the sulfonamide molecule and the NH_3 group of the anilinium ion [N···Cl = 3.135 (3)–3.196 (2) Å and N—H···Cl = 151–167°] are involved. This hydrogen-bonded chain contains two independent $R_4^2(8)$ rings and each chloride ion acts as an acceptor of four hydrogen bonds.

Comment

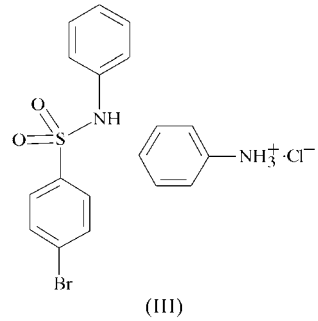
In a project aimed at relating crystal structure to molecular structure, which we term structural systematics, large numbers of related molecules are synthesized and their crystal structures determined. For this purpose, it is essential to choose compounds that can be synthesized readily, and for well known reactions it is usually easy to determine whether this is the case. By contrast, it is not possible to forecast whether the products will crystallize easily with sufficient size and quality for single-crystal diffraction, except in a very general and imperfect way by experience of crystallizing large numbers of



(I)

related compounds. In this project, over 100 benzenesulfonamides of the general structure (I) have been synthesized, where *X* and *Y* are H, CH_3, F, Cl, Br, I, CF_3, CN, NO_2 and MeO, and, additionally, *Y* is ethynyl. These sulfonamides generally crystallize more readily than the related carboxamides, chalcones, or pyridine and other heterocyclic analogues, the structural systematics of which are also under investigation. The syntheses are usually trivial. In a few cases, the not unexpected disulfonyl by-product has been isolated. Adjustment of the reactant quantities and reaction conditions has allowed the required product to be formed exclusively.

In only one case out of more than 100 samples of this set, and out of many hundreds of examples in the extended set, has an unexpected product been encountered. This was during the synthesis intended to produce compound (II), where *X* = Br and *Y* = H. This compound is difficult to crystallize because of its extreme solubility in most solvents, including hydrocarbons, and the result of evaporative crystallization is generally a viscous syrup. During an attempted crystallization of (II) from toluene, novel crystals were encountered which were initially thought to be the toluene solvate of the hydrochloride of (II). This seemed chemically improbable, because of the weak basicity of sulfonamides, although it is possible for favourable crystal structures of salts and adducts to contradict expectations derived from solution-determined basicities. Refinement of the structure led to the elucidation of the composition as the anilinium chloride adduct, (III), of the required sulfonamide, (II).



(III)

The bond lengths and angles of the sulfonamide molecule (Fig. 1) are in accordance with those in previously reported molecules of the general structure (I) [*X* = Cl and *Y* = Br, and *X* = Br and *Y* = H (Rérat, 1969); *X* = *Y* = MeO (Pokrywiecki *et al.*, 1973); *X* = I and *Y* = NO_2, and *X* = NO_2 and *Y* = I (Kelly *et al.*, 2002)]. Our own systematic investigation of crystal structures formed by molecules (I) has shown that they are generally dominated by intermolecular N—H···O hydrogen-bond interactions between the amine group and one sulfonyl O atom, with the exception of only a few cases where *X* or *Y* is CN or NO_2. These interactions generate two distinct supramolecular synthons, *viz.* a dimer resulting in the formation of $R_2^2(8)$ rings (Bernstein *et al.*, 1995) and a chain motif. These typical N—H···O chains also occur in the single-component structure of sulfonamide (II), to be published elsewhere. However, the formation of either of the two N—H···O bond motifs is prevented in cocrystal (III) by the presence of the chloride ion. Instead, sulfonamide molecules are linked by N—H···Cl hydrogen bonds to chloride ions. Furthermore, Cl^- is at the same time involved in another three N—H···Cl

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bonding interactions with the ammonium groups of three different anilinium ions. In turn, each anilinium ion is connected *via* its ammonium group to three Cl^- ions (Fig. 2). As a result, two crystallographically independent hydrogen-bonded rings are formed, which are both of the $R_4^2(8)$ type. Each ring has a centre of inversion, and adjacent rings, which are crystallographically independent, *viz.* $\cdots$Cl1$\cdots$H2—N2—H4$\cdots$Cl1$\cdots$ and $\cdots$Cl1$\cdots$H3—N2—H4$\cdots$Cl1$\cdots$, have a common N2—H4$\cdots$Cl1 edge. Thus, a corrugated ladder structure is obtained. This one-dimensional infinite structure propagates parallel to [100]. It consists of two antiparallel strands of three-connected nodes, composed alternately by chloride ions and ammonium groups of the anilinium ions. Additionally, each chloride node has a fourth connection to one sulfonamide molecule, and neighbouring sulfonamide molecules attached to the same strand of the ladder are related by translation symmetry. By contrast, two molecules connected to chloride nodes located in different strands of the same ladder are related by inversion symmetry.

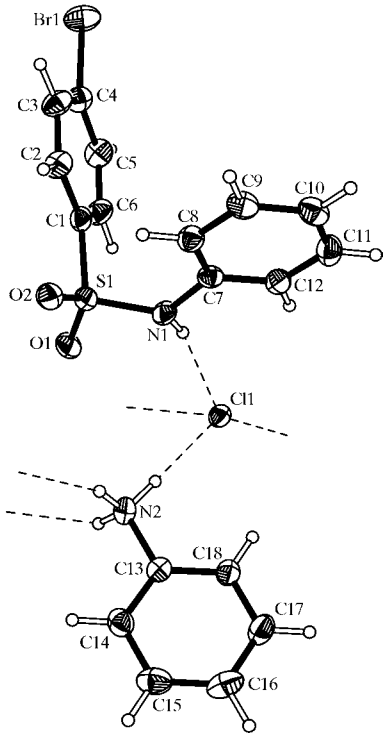

Figure 1
The asymmetric unit of (III), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

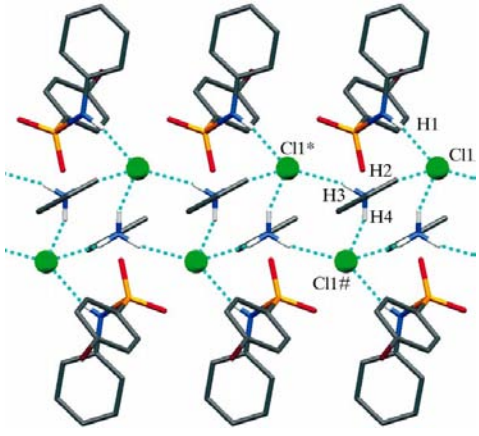

Figure 2
The one-dimensional hydrogen-bonded net (ladder) between sulfonamide molecules, anilinium cations and chloride anions in (III). Hydrogen bonds are indicated by dashed lines. Atoms marked with an asterisk (*) or hash (#) are at the symmetry positions ($x-1, y, z$) and ($-x+1, -y, -z+1$), respectively.

For the three H atoms in the ammonium group of the anilinium ion, the structure of (III) contains one chloride ion as a potential hydrogen-bond acceptor, and ignoring the sulfonamide molecule, a net consisting of three-connected chloride and ammonium nodes is formed as a result. The same situation was found in the structure of anilinium chloride (López-Duplá *et al.*, 2003), from which, however, a fundamentally different topology arises. Here, a two-dimensional hydrogen-bonded net with (6,3)-topology (Wells, 1977) is formed in which the two types of nodes alternate. By contrast, the ladder motif observed in (III) occurs in other related bromide and iodide structures, such as 2-methyl-4-nitro-

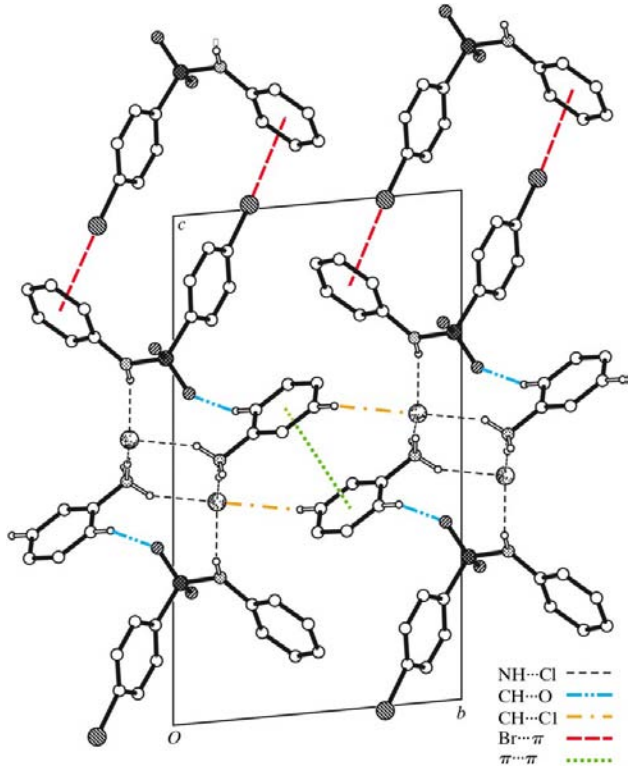

Figure 3
Part of the crystal structure of (III), consisting of two complete N—H$\cdots$Cl-bonded ladders (lower section) and portions of another two such units, showing the interplay between different types of intermolecular interaction. The structure is viewed in the direction of the translation vector of the N—H$\cdots$Cl hydrogen-bonded chains. Only H atoms involved in contacts listed in Table 1 are shown.

anilinium iodide (Lemmerer & Billing, 2006), while the high- and low-temperature forms of anilinium bromide (Sakai & Terauchi, 1981; Fecher *et al.*, 1981) and anilinium iodide (Fecher & Weiss, 1986) produce a disordered derivative of the same ladder.

Each N—H···Cl-bonded ladder exhibits additional internal close C14—H14···O1 contacts between anilinium ions and sulfonamide molecules (Table 1). There is also a set of two close Br···π contacts between two sulfonamide molecules which belong to neighbouring ladders related by translation along the *c* axis. The separation between Br and the centroid of the benzene ring is 3.52 Å. Furthermore, the anilinium ions of two neighbouring ladders related by translation along the *b* axis are π–π stacked (centroid separation = 4.01 Å). The same two units are also linked by two sets of C—H···Cl contacts between their anilinium and chloride ions (Table 1). All described close contacts are shown in the packing diagram (Fig. 3).

The origin of the anilinium chloride resulting from part of the reactant aniline acting as a proton acceptor is readily understood. It is surprising that it was not eliminated during the normal work-up procedure of evaporation to small volume to remove the pyridine and pyridine hydrochloride, followed by puddling with water to effect solidification. If this persistence into the final product is due to the particular stability of the crystal structure, then it is surprising that analogous compounds have not been frequently encountered during this project.

Experimental

4-Bromobenzenesulfonyl chloride (0.255 g, 1 mmol) was added to a solution of aniline (0.093 g, 1 mmol) in pyridine (3 ml). The orange–red colour that formed was discharged on boiling. After boiling for 30 min, the solution was evaporated to a small bulk under nitrogen until white fumes of pyridine hydrochloride began to appear. The cooled residue was treated with water and scratched with a rod until it solidified. The product was filtered off, dissolved in ethanol (5 ml) and allowed to evaporate to a syrup. The product was taken up in toluene (4 ml) and allowed to evaporate until crystals appeared. The elongated prisms were identified as the anilinium chloride adduct of 4-bromo-*N*-phenylbenzenesulfonamide, and the smaller plates as 4-bromo-*N*-phenylbenzenesulfonamide itself.

Crystal data

$C_6H_8N^+\cdot Cl^-\cdot C_{12}H_{10}BrNO_2S$
M_r = 441.76
Triclinic, $P\overline{1}$
a = 5.6705 (4) Å
b = 9.9954 (7) Å
c = 17.3234 (12) Å
α = 83.137 (4)°
β = 81.655 (4)°
γ = 77.163 (3)°
V = 943.31 (11) Å^3
Z = 2
D_x = 1.555 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 2.44 mm^{-1}
T = 120 (2) K
Prism, colourless
0.50 × 0.20 × 0.20 mm

Data collection

Bruker–Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.359, T_{max} = 0.615
8226 measured reflections
3286 independent reflections
2646 reflections with $I > 2\sigma(I)$
R_{int} = 0.039
θ_{max} = 25.1°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.088
S = 1.04
3286 reflections
248 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.045P)^2 + 0.0802P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.37 e Å^{-3}
$\Delta\rho_{min}$ = −0.55 e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0060 (13)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···Cl1	0.878 (14)	2.332 (18)	3.157 (3)	157 (3)
N2—H2···Cl1	0.91	2.30	3.196 (2)	167
N2—H3···Cl1^{i}	0.91	2.25	3.135 (3)	163
N2—H4···Cl1^{ii}	0.91	2.33	3.152 (2)	151
C14—H14···O1^{iii}	0.95	2.39	3.307 (3)	163
C17—H17···Cl1^{iv}	0.95	2.85	3.661 (3)	144

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

All H atoms were located in difference maps. The position of the H atom attached to N1 was refined with the N—H distance restrained to 0.900 (15) Å. All other H atoms were treated as riding, with C—H distances of 0.95 Å and N—H distances of 0.91 Å. All U_{iso}(H) values were refined freely.

Data collection: *COLLECT* (Hooft, 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Bruker, 1998) and *MERCURY* (Macrae *et al.*, 2006).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ3025). Services for accessing these data are described at the back of the journal.

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