Polysulfonylamines, CLXXXV [1]. Hydrogen Bonding or Halogen Bonding? The Supramolecular Structures of 3-Bromoanilinium and 4-Bromoanilinium Di(4-bromobenzolsulfonyl)amides

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This study characterizes the supramolecular synthons that dominate the interionic organization of 3-bromoanilinium di(4-bromobenzolsulfonyl)amide (1) and the corresponding 4-bromoanilinium salt (2) in their respective crystal structures (1: orthorhombic, Pbca, Z′ = 1; 2: monoclinic, P2₁/n, Z′ = 1). Although these compounds contain N⁺–H donors and C–Br groups in equal numbers, their ion packings are exclusively governed by classical, and mostly bifurcated, hydrogen bonds of the type N⁺–H···O=S/N⁻, whereas halogen bonding C–Br···O=S/N⁻ is absent from both structures. The isomerism of the cations, which is the only chemical difference between 1 and 2, drives the hydrogen bonds to form a network that is two-dimensional in 1, but one-dimensional in 2. The resulting layers or strands are coherently built up from hydrophilic internal regions consisting of NH₃⁺ and (SO₂)₂N⁻ groups, external hydrophobic domains of phenyl rings, and peripherically projecting bromine atoms. As the hydrophobic groups from adjacent layers or strands do not interdigitate, the bromine atoms are sterically available to form short Br···Br interlayer contacts of quasi-type I in 1 and inversion symmetric Br₄ interstrand quadrilaterals in 2. The results of a database search for quadrilateral (C–Br)₄ synthons are also presented.

Key words: Anilinium, Hydrogen Bonding, Interhalogen Bonding, Sulfonamides