Polysulfonylamine, CXLIII [1]. Rolle schwacher Wasserstoffbrücken (C–H⋯O) in den Kristallstrukturen von 2,6-Dimethylpyridinium-, 1-Hydroxy-pyridinium- und Imidazolium-dimesylamid

Polysulfonylamines, CXLIII [1]. Role of Weak Hydrogen Bonds (C–H⋯O) in the Crystal Structures of 2,6-Dimethylpyridinium, 1-Hydroxypyridinium and Imidazolium Dimesylamide

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Di(methanesulfonyl)amide, Weak Hydrogen Bonding, Very Short Heteronuclear Hydrogen Bond

In order to study hydrogen bonding networks in ionic crystals, low-temperature X-ray structures were determined for three onium salts of general formula BH+(MeSO₂)₂N⁻, where BH+ is 2,6-dimethylpyridinium (1; monoclinic, space group P2₁/c, Z' = 1), 1-hydroxypyridinium (2; triclinic, P₁, Z' = 1), or imidazolium (3; monoclinic, Cc, Z' = 1). The asymmetric units consist of cation–anion pairs assembled in 1 and 3 by ordinary N+–H⋯N hydrogen bonds, in 2 by a very short N+–O–H⋯N⁻ bond belonging to the class (+/−)CAHB [H⋯O 148(3), O⋯N 253.5(2) pm, O–H⋯N 175(3)°]. The second N–H donor of the imidazolium ion is involved in a nearly symmetric N–H(⋯O)₂ three-centre bond to two different anions. In the pyridine derivatives, the (MeSO₂)₂N⁻ ions are associated via short C(sp³)–H⋯O contacts to form a three-dimensional framework of corrugated and cross-linked layers (1) or an assembly of discrete corrugated layers (2). As a common feature, these anion substructures are pervaded by hexagonal channels parallel to x, each one accommodating two stacks of cations that are linked to the channel walls by the unique strong hydrogen bond and a set of short C(sp³)–H⋯O contacts; moreover, cations drawn from adjacent stacks in structure 2 create inversion-symmetric dimers based upon a short C(sp³)–H⋯O(H)–N interaction. In contrast, the structure of 3 displays planar anion layers assembled by short C(sp³)–H⋯O contacts, intercalating the cations with their ring planes perpendicular to the layer planes and binding them by means of the strong hydrogen bonds and three C(sp³)–H⋯O interactions. All C–H⋯O taken into consideration have normalized parameters d(H⋯O) ≤ 267 pm and θ(C–H⋯O) ≥ 121°.