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Hydrogen Bonding in Crystalline Onium Dimesylamides: Six Systematically Varied sec.-Ammonium Dimesylamides Exhibiting Six Different Zero-, One-, or Two-Dimensional Hydrogen Bonding Patterns

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In order to examine packing preferences and hydrogen bond patterns in secondary ammonium salts, low-temperature X-ray analyses were conducted for six compounds of general formula \( \text{R}_2\text{NH}^+\text{(MeSO}_2\text{)}_2\text{N}^- \), where \( \text{R}_2\text{NH}^+ = \text{Me}_2\text{NH}^+ (1, \text{triclinic, space group } P\bar{1}), \text{MeEtNH}^+ (2, \text{monoclinic, } P2_1/c), \text{Et}_2\text{NH}^+ (3, \text{triclinic, } P\bar{1}), \text{pyrrolidinium} (4, \text{triclinic, } P\bar{1}), \text{piperidinium} (5, \text{monoclinic, } C2/c) \) or morpholinium (6, monoclinic, \( P2_1/c \)). Throughout the series, the constant anion retains a rigid conformation approximating to \( C_2 \) symmetry and thus provides a geometrically reliable set of five potential hydrogen bond acceptors. Nevertheless, the six compounds exhibit a variety of unpredictable packing patterns, showing that, in unfavourable cases, the steric demands of molecular fragments not involved in hydrogen bonding can substantially alter the structure of a family of ionic crystals. In the present structures, the \( \text{NH}_2^+ \) donor groups form hydrogen bonds \( \text{N}^+\cdots\text{H}\cdots\text{N}^-/\text{O} \) to two (3–6) or three (1, 2) adjacent anions. The occurrence of various two-, three- and four-centre hydrogen bonds leads to six different patterns, resulting in cation–anion layers (1, 2), discrete formula unit dimers (3, 4) or cation–anion chains (5, 6); in the morpholinium salt 6, these chains are associated into layers by a weak \( \text{N}^+\cdots\text{H}\cdots\text{O(cation)} \) interaction. In each of the crystal packings, short \( \text{C}–\text{H}\cdots\text{O} \) contacts with \( \text{H}\cdots\text{O} \leq 270 \text{ pm} \) and \( \text{C}–\text{H}\cdots\text{O} \geq 130^\circ \) are observed.