

Wasserstoffbrücken in kristallinen Onium-dimesylamiden: Ein robustes Achtring-Synthon in Koexistenz mit einem dritten Wasserstoffbrückenmotiv – Cyclodimere, Ketten, supramolekulare Bindungsisomere und ein fünffach verwobenes dreidimensionales (C–H⋯O)-Netzwerk

Polysulfonylamines, CXXVI [1]

Hydrogen Bonding in Crystalline Onium Dimesylamides: A Robust Eight-Membered Ring Synthone in Coexistence with a Third Hydrogen Bonding Motif – Cyclodimers, Chains, Supramolecular Linkage Isomers, and a Quintuply Interwoven Three-Dimensional C–H⋯O Network

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Z. Naturforsch. **55b**, 738–752 (2000); eingegangen am 23. März 2000

Di(methanesulfonyl)amide, Onium Cation, Supramolecular Isomerism

As an exercise in crystal engineering, low-temperature X-ray structures were determined for six rationally designed ionic solids of general formula $\text{BH}^+(\text{MeSO}_2)_2\text{N}^-$, where BH^+ is 2-aminopyridinium (**2**, monoclinic, space group $P2_1/c$, $Z = 4$), 2-aminopyrimidinium (**3**, orthorhombic, $Pbca$, $Z = 8$), 2-aminothiazolium (**4**, orthorhombic, $Pbcn$, $Z = 8$), 2-amino-6-methylpyridinium (**5**, solvated with 0.5 H_2O , monoclinic, $C2/c$, $Z = 8$), 2-amino-1,3,4-thiadiazolium (**6**, triclinic, $P1$, $Z = 2$), or 2-amino-4,6-dimethylpyrimidinium (**7**, orthorhombic, $Fdd2$, $Z = 16$). The onium cations in question exhibit a trifunctional hydrogen-bond donor sequence $\text{H}-\text{N}(\text{H}^*)-\text{C}(\text{sp}^2)-\text{N}-\text{H}$, which is complementary to an $\text{O}-\text{S}(\text{sp}^3)-\text{N}$ fragment of the anion and simultaneously expected to form a third hydrogen bond *via* the exocyclic $\text{N}-\text{H}^*$ donor. Consequently, all the crystal packings contain cation-anion pairs assembled by an $\text{N}-\text{H}\cdots\text{N}$ and an $\text{N}-\text{H}\cdots\text{O}$ hydrogen bond, these substructures being mutually associated through an $\text{N}-\text{H}^*\cdots\text{O}$ bond. For the robust eight-membered ring synthone within the ion pairs [graph set $\text{N}_2 = \text{R}_2^2(8)$, antidromic], two supramolecular isomers were observed: In **2** and **3**, $\text{N}-\text{H}\cdots\text{N}$ originates from the ring NH donor and $\text{N}-\text{H}\cdots\text{O}$ from the exocyclic amino group, whereas in **4–7** these connectivities are reversed. The third hydrogen bond, $\text{N}-\text{H}^*\cdots\text{O}$, leads either to chains of ion pairs (generated by a 2_1 transformation in **2–4** or by a glide plane in **5**) or to cyclic dimers of ion pairs (C_2 -symmetric in **6**, C_2 -symmetric in **7**). The overall variety of motifs observed in a small number of structures reflects the limits imposed on the prediction of hydrogen bonding patterns. Owing to the excess of potential acceptors over traditional hydrogen-bond donors, several of the structures display prominent non-classical secondary bonding. Thus, the cyclodimeric units of **6** are associated into strands through short antiparallel $\text{O}\cdots\text{S}(\text{cation})$ interactions. In the hemihydrate **5**, two independent $\text{C}-\text{H}(\text{cation})\cdots\text{O}$ bonds generate a second antidromic $\text{R}_2^2(8)$ pattern, leading to sheets composed of $\text{N}-\text{H}\cdots\text{N}/\text{O}$ connected catemers; the water molecules are alternately sandwiched between and $\text{O}-\text{H}\cdots\text{O}$ bonded to the sheets to form bilayers, which are cross-linked by a third $\text{C}-\text{H}(\text{cation})\cdots\text{O}$ contact. The roof-shaped cyclodimers occurring in **7** occupy the polar C_2 axes parallel to z and build up hollow $\text{C}_{\text{ar}}-\text{H}\cdots\text{O}$ bonded tetrahedral lattices; in order to fill their large empty cavities, five translationally equivalent lattices mutually interpenetrate.