Polysulfonylamines, CL [1]. Hydrogen Bonding in Crystalline Onium Dimesylamides: A Robust Eight-Membered Ring Synthon in the Structures of Methyluronium and 1,1-Dimethyluronium Dimesylamide

Dagmar Henschel, Thomas Hamann, Oliver Moers, Armand Blaschette and Peter G. Jones

Institut für Anorganische und Analytische Chemie der Technischen Universität, Postfach 3329, D-38023 Braunschweig

Sonderdruckanforderungen an Prof. Dr. A. Blaschette oder Prof. Dr. P. G. Jones. Fax: +49(0) 5313915387, E-mail: p.jones@tu-bs.de

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Methyluronium dimesylamide (1) and 1,1-dimethyluronium dimesylamide (2) have been prepared by proton transfer reactions of the strong nitrogen acid HN(SO2Me)2 with the corresponding ureas and characterized by low-temperature X-ray diffraction (1: orthorhombic, space group $P2_12_12_1$, $Z' = 1$; 2: orthorhombic, $Pna2_1$, $Z' = 2$). Compound 2 appears to be the first crystallographically established 1,1-dimethyluronium salt. As a common feature, the three independent formula units consist of ion pairs held together by an eight-membered ring synthon $[\bar{N} = R_3^2(8), \text{antidromic}]$ constructed from a $\text{syn,syn}$-sequence $\text{H} - \text{O} - \text{C}(\text{sp}^2) - \text{N} - \text{H}$ of the cation and a $\text{V}$-shaped $\text{O} - \text{S}(\text{sp}^3) - \text{N}$ fragment of the anion via homonuclear two-centre hydrogen bonds. The surplus N–H donors form hydrogen bonds to O=S acceptors in adjacent formula units, leading to a three-dimensional network (1) or a pseudo-$2_1$ symmetric helical catemer of alternatingly inequivalent formula units (2). In both structures, the activated methyl groups give rise to numerous short interionic C–H···O contacts, the more prominent of which are analyzed in terms of weak hydrogen bonding [cut-off criteria: $d(\text{H}···\text{O}) \leq 270$ pm, $\theta(\text{C}–\text{H}···\text{O}) \geq 130^\circ]$. 