

Polysulfonylamine, CXIX [1, 2]

Wasserstoffbrücken in kristallinen Onium-dimesylamiden: Ein antidromes Achtringmuster als robustes supramolekulares Synthon – Drei prototypische Strukturen

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Hydrogen Bonding in Crystalline Onium Dimesylamides: An Antidromic Eight-Membered Ring Pattern as a Robust Supramolecular Synthon – Three Prototypical Structures

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Syntheses and low-temperature X-ray structures are reported for three ionic solids of general formula $\text{BH}^+(\text{MeSO}_2)_2\text{N}^-$, where BH^+ is 3,4,6,7,8,9-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidinium (**1**, monoclinic, space group $P2_1/c$), $\text{N,N}'$ -diphenylformamidinium (**2**, monoclinic, $P2_1/c$), or 2-phenylaminopyridinium (**3**, triclinic, $P\bar{1}$, two independent formula units). As a common feature, the onium cations in question exhibit a difunctional hydrogen-bond donor sequence $\text{H}-\text{N}-\text{C}(\text{sp}^2)-\text{N}-\text{H}$ geometrically complementary to an $\text{O}-\text{S}-\text{N}$ fragment of the anion. Consequently, the three crystal packings consist of discrete cation–anion pairs (formula units) assembled by an $\text{N}-\text{H}\cdots\text{N}$ and an $\text{N}-\text{H}\cdots\text{O}$ hydrogen bond. In both independent ion pairs of **3**, the $\text{N}-\text{H}\cdots\text{N}$ bond originates from the pyridinium centre and the $\text{N}-\text{H}\cdots\text{O}$ bond from the amino group. The eight-membered ring [graph set $\text{N}_2 = \text{R}_2^2(8)$, antidromic] that results in all these prototypical structures has potential as a new and robust supramolecular synthon. In each case, short $\text{C}-\text{H}\cdots\text{O}$ contacts with $\text{H}\cdots\text{O} \leq 260$ pm and $\text{C}-\text{H}\cdots\text{O} \geq 140^\circ$ are present; in **2**, two $\text{C}_{\text{ar}}-\text{H}\cdots\text{O}$ hydrogen bonds are assisted by a $\text{C}(\text{formyl})-\text{H}\cdots\text{O}$ contact and a $\pi-\pi$ interaction to create a centrosymmetric formula unit dimer.