

# Polysulfonylamine, CLXXIII [1]. Intermolekulare Wechselwirkungen in kristallinen Di(organosulfonyl)aminen. – Teil 2 [2]. Strukturvergleich für Di(4-X-benzolsulfonyl)amine mit X = Fluor, Chlor, Brom oder Methyl

Polysulfonylamines, CLXXIII [1]. Intermolecular Interactions in Crystalline Di(organo-sulfonyl)amines. Part 2 [2]. Comparing the Structures of Di(4-X-benzenesulfonyl)amines, where X is Fluorine, Chlorine, Bromine, or Methyl

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Low-temperature X-ray structures of the following di(4-X-benzenesulfonyl)amines,  $\text{HN}(\text{SO}_2\text{-C}_6\text{H}_4\text{-X})_2$ , are compared in order to study the effects of the 4-substituents on the molecular packings: X = F (**1**, monoclinic,  $C2/c$ ,  $Z' = 1$ ), X = Cl (**2**, monoclinic,  $C2/c$ ,  $Z' = 1/2$ , N-H bonds lying on twofold rotation axes), X = Me (**3**, orthorhombic,  $Pbca$ ,  $Z' = 1$ ), X = Br (**4A**, monoclinic,  $P2_1/c$ ,  $Z' = 1$ ), X = Br (**4B**, monoclinic,  $P2_1/c$ ,  $Z' = 2$ ). As a common feature, the molecules of the halogen compounds, including two polymorphs of **4**, are associated into catemers by strong hydrogen bonds of the type  $\text{N-H}\cdots\text{O}$  in **1**, **4A** and **4B** or  $\text{N-H}(\cdots\text{O})_2$  in **2**. These molecular chains are assembled in the crystal structures *via* different packing modes, which underline the well-known correlation between the atomic number of halogen atoms and their propensity to form halogen bonds. Thus, the structure of **1** is devoid of short  $\text{C-F}\cdots\text{O/N}$  contacts, but close  $\text{F}\cdots\text{F}$  contacts are tolerated, whereas in **2** each catemer is connected to four parallel congeners by long and bifurcated  $\text{C-Cl}(\cdots\text{O})_2$  bonds, and both polymorphs of **4** display layers in which the molecules are connected by  $\text{N-H}\cdots\text{O}$  bonds in one and by relatively short and approximately linear  $\text{C-Br}\cdots\text{O}$  interactions in the other dimension. Despite the alleged steric equivalence of methyl and chloro substituents (“chloro-methyl exchange rule”), the packing architecture of the methyl compound **3** is not related to any of the preceding structures. In this case, the  $\text{N-H}\cdots\text{O}$  bonding leads to centrosymmetric cyclodimers, which pack in such a way that each methyl group is located between two oxygen atoms and above the face of an aromatic ring in a topology consistent with  $\text{C-H}\cdots\text{O}$  and  $\text{C-H}\cdots\text{C}(\pi)$  bonding. All the structures are pervaded by weak  $\text{C}_{\text{ar}}\text{-H}\cdots\text{O}$  hydrogen bonds; moreover, **1** displays a short  $\text{C-H}\cdots\text{F}$  hydrogen bond and a  $\text{C-F}\cdots\text{C}(\pi)$  interaction, and  $\pi$ -stacking of aromatic rings is observed in **1**, **3** and **4B**.

*Key words:* Hydrogen Bonding, Halogen Bonding,  $\pi\cdots\pi$  Stacking,  $\text{C-H/C-F}\cdots\text{C}(\pi)$  Interactions, Sulfonamides