Polysulfonylamine, CLXXV [1]. Intermolekulare Wechselwirkungen in kristallinen Di(organosulfonyl)aminen. Teil 3 [2]. Supramolekulare Strukturen von Di(benzolsulfonyl)amin, (Benzolsulfonyl)(methansulfonyl)amin und Di(ethansulfonyl)amin

Polysulfonylamines, CLXXV [1]. Intermolecular Interactions in Crystalline Di(organosulfonyl)-amines. Part 3 [2]. Supramolecular Structures of Di(benzenesulfonyl)amine, (Benzenesulfonyl)-(methanesulfonyl)amine, and Di(ethanesulfonyl)amine

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Low-temperature X-ray structures of the following di(organosulfonyl)amines, $HN(SO_2R)(SO_2R')$, are compared in order to study the packing effects of group-specific intermolecular interactions: R = R' = phenyl (**1**, monoclinic, $P2_1/c$, $Z' = 1$); R = phenyl, R' = methyl (**2**, monoclinic, $P2_1/n$, $Z' = 1$); R = R' = ethyl (**3**, monoclinic, $P2_1/c$, $Z' = 1$). The molecules of each compound are associated into catemers by N-H···O hydrogen bonds of graph set C(4). These catemers form molecular layers *via* distinctive cross-linking modes, which underline the specific propensity of the organic groups to establish directional intermolecular interactions. Thus, the packing of **1** displays *striated* layers constructed from polar strands of hydrogen-bonded $HN(SO_2)_2$ fragments, and apolar strands, in which $(phenyl)_4$ supercycles based upon C-H···C(π) interactions are fused into a linear superpolymer by $\pi\cdots\pi$ stacking-dimer motifs; moreover, C-H···O hydrogen bonds occur between adjacent intra-layer strands and between adjacent layers. Molecule **1** features conformational anomalies induced by the high geometric demands of the supramolecular phenyl pattern. In contrast to **1**, compound **2** forms *lamellar* layers comprising an internal polar lamella of N-H···O connected $HN(SO_2)_2$ fragments as well as inductively activated methyl groups, and apolar peripheral regions of phenyl rings. The methyl groups are engaged with all their hydrogen atoms in a two-dimensional C-H···O network, whereas the protruding phenyl rings of adjacent layers are interlocked in such a way that short C-H···O inter-layer contacts are created. On account of the reduced phenyl population as compared to **1**, C-H···C(π) and $\pi\cdots\pi$ stacking interactions are absent from the crystal structure of **2**. Structure **3** finally consists of *homogeneous* layers, in which the N-H···O based catemers are both re-enforced and cross-linked by C-H···O bonds originating from the four activated methylene hydrogen atoms, whereas adjacent layers are separated by methyl-oxygen contacts with H···O distances longer than the van der Waals limit.

Key words: N-H···O/C-H···O Hydrogen Bonding, C-H···C(π) Interactions, $\pi\cdots\pi$ Stacking, Layered Compounds, Sulfonamides