Polysulfonylamine, CLXXIX [1]. Intermolekulare Wechselwirkungen in kristallinen Di(organosulfonyl)aminen. Teil 4 [2]. Di(4-iodbenzolsulfonyl)amin und zwei Methylpyridinium-di(4-iodbenzolsulfonyl)amide: Iod-Sauerstoff- *vs.* Iod-Iod-Wechselwirkungen

Polysulfonylamines, CLXXIX [1]. Intermolecular Interactions in Crystalline Di(organosulfonyl)amines. Part 4 [2]. Di(4-iodobenzenesulfonyl)amine and Two Methylpyridinium Di(4-iodobenzenesulfonyl)amides: Iodine-Oxygen *vs*. Iodine-Iodine Interactions

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Z. Naturforsch. **2007**, *62b,* 1157 – 1166; received March 5, 2007

Low-temperature X-ray structures and crystal packing arrangements are presented for di(4-iodobenzenesulfonyl)amine (**4**, monoclinic, $P2_1/c$, $Z' = 1$, isostructural to a previously described dimorph of the corresponding bromo homologue), 2,4-dimethylpyridinium di(4-iodobenzenesulfonyl)amide (**5**, monoclinic, $P2_1/n$, $Z' = 1$, isostructural to the corresponding bromo compound), and 3-methylpyridinium di(4-iodobenzenesulfonyl)amide (**6**, orthorhombic, $Pna2_1$, $Z' = 1$). The packing of **4** consists of non-lamellar layers, in which the molecules are connected by N–H···O hydrogen bonds in one and by $I^{\delta+}\cdots O^{\delta-}$ interactions in the other dimension. Structure **5** involves strands of formula units, whereby the anions form catemers *via* $I^{\delta+}\cdots O^{\delta-}$ interactions and the cations are isotactically connected to the anion backbone by an N^+–H(···O)$_2$ three-centre bond. Short I···I contacts are absent from structures **4** and **5**. In contrast, structure **6** displays lamellar layers comprising an inner lamella of cations and N(SO$_2$)$_2$ groups connected by an N^+–H···N^- two-centre bond, and peripheral regions of 4-iodophenyl rings. Thus, the iodine atoms are efficiently shielded from the oxygen atoms, but in appropriate positions to form $I^{\delta+}\cdots I^{\delta-}$ interlayer contacts. Each structure is reinforced by a parallel-displaced $\pi\cdots\pi$ stacking arrangement of aromatic rings and an abundance of short C–H···A contacts (A = acceptor).

Key words: Hydrogen Bonding, Iodine-Oxygen Interactions, Iodine-Iodine Interactions, Sulfonamides, Nitrogen Heterocycles