Polysulfonylamine, CLXIX [1]. Intermolekulare Wechselwirkungen in kristallinen Di(organosulfonyl)aminen. Teil 1. Di(4-brombenzolsulfonyl)amin: Zwei Konformationspolymorphe und Strukturverwandtschaft eines Polymorphs mit dem entsprechenden 2,4-Dimethylpyridinium-Salz

Polysulfonylamines, CLXIX [1]. Intermolecular Interactions in Crystalline Di(organosulfonyl)-amines. Part 1. Di(4-bromobenzenesulfonyl)amine: Two Conformational Polymorphs and the Structural Relationship of one Polymorph to the Corresponding 2,4-Dimethylpyridinium Salt

Virginia Lozano, Oliver Moers, Peter G. Jones und Armand Blaschette

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

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

Z. Naturforsch. **59b,** 661 – 672 (2004); eingegangen am 11. Februar 2004

Two crystal structures (polymorphs) of di(4-bromobenzenesulfonyl)amine (**1**), as determined by low-temperature single-crystal X-ray diffraction, are reported: Form **A**, monoclinic, $P2_1/c$, $Z' = 1$; form **B**: monoclinic, $P2_1/c$, $Z' = 2$. In **A**, the molecule adopts an extended conformation approximating to C_2 symmetry, whereas the two independent molecules of form **B** display a folded hair-pin conformation with pseudo-mirror symmetry [torsion τ(C-S$\cdots$S'-C') and intercentroid distance d_{IC} of the aromatic rings in **A**: 173.2° and 750.8 pm, in **B**: $-5.4/-8.90°$ and 364.1/366.5 pm]. The packings of both polymorphs consist of layers, in which the molecules are connected by N-H$\cdots$O hydrogen bonds in one and by Br$\cdots$O interactions in the other dimension. The 1:1 onium salt (**2**; monoclinic, $P2_1/n$, $Z' = 1$) produced on N-deprotonation of **1** with 2,4-dimethylpyridine is structurally related to **B**. Its packing involves strands of formula units, whereby the anions retain the folded conformation ($\tau = 5.8°$, $d_{IC} = 372.5$ pm) and perfectly mimic the catemeric Br$\cdots$O pattern of **B**, while the cations are isotactically connected to the anion backbone *via* an N-H($\cdots$O)$_2$ three-centre bond. In all structures, a three-dimensional network of weak hydrogen bonds C-H$\cdots$A (A = O, in **2** also N$^-$) and C-H$\cdots$Br contacts supports the controlling N-H$\cdots$O and Br$\cdots$O interactions; moreover, an intermolecular ($\pi\cdots\pi$) stacking dimer of the type phenyl/phenyl and a ($\pi\cdots\pi$) stacking trimer of the type phenyl/pyridinium/phenyl have been identified in **A** and **2**, respectively. None of the structures exhibits very short bromine-bromine contacts suggestive of specific attractive forces.

Key words: Conformational Polymorphism, Hydrogen Bonding, Bromine-Oxygen Interactions, Sulfonamides, Nitrogen Heterocycles