Zwischenmolekulare Wechselwirkungen in den Kristallstrukturen von 4-Halogenbenzolsulfonamiden (Halogen = Fluor, Chlor, Brom, Iod) und 4-Methylbenzolsulfonamid

Intermolecular Interactions in the Crystal Structures of 4-Halobenzenesulfonamides (Halogen = Fluorine, Chlorine, Bromine, Iodine) and 4-Methylbenzenesulfonamide

Eva-Maria Zerbe, 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. **60b,** 125 – 138 (2005); eingegangen am 14. September 2004

Low-temperature single-crystal X-ray structures of the following 4-X-benzenesulfonamides have been studied in order to compare the effects of the 4-substituents on the molecular packings: X = F (**1**, orthorhombic, *Pbca*, $Z' = 1$, structure previously reported), X = Cl (**2**, monoclinic, $P2_1/n$, $Z' = 1$), X = Br (**3**, isostructural with **2**), X = Me (**4**, isomorphous with **2** and **3**, room-temperature structure previously reported, accurate redetermination in this work), X = I (**5**, monoclinic, *Pc*, $Z' = 2$ molecules with markedly different conformations). As a common feature, the five structures display molecular layers comprising an internal polar lamella of H_2NSO_2 groups engaged in N-H···O hydrogen bonding, and hydrophobic peripheral regions consisting of the 4-X-substituted phenyl rings. Whereas each molecule in **1 – 4** is linked to four adjacent congeners by ordinary two-centre hydrogen bonds, the sterically demanding iodo substituent in **5** causes all N-H···O interactions to split up into longer N-H(···O)$_2$ three-centre bonds that are used to connect each molecule to six adjacent molecules. Important packing differences between **1** and the other structures appear to emanate from the high electronegativity of fluorine. In **2 – 5**, the polar lamellae are approximately planar, and the aromatic groups protrude obliquely (**2 – 4**) or vertically (**5**) from the lamellae to form translation-generated parallel stacks separated by broad voids. Contiguous layers are packed *via* stack-void interlocking, thus creating high packing density and, concomitantly for **2**, **3** and **5**, interlayer halogen bonds of the type Cl···O, Br···O or I···N, respectively; none of the four structures exhibits $\pi\cdots\pi$ stacking interactions between aromatic rings or short halogen-halogen contacts. This simple packing architecture does not hold in the case of **1**. Here, the polar lamella adopts a zigzag profile with acute angles of *ca.* 60°, allowing high packing density to be achieved by intralayer $\pi\cdots\pi$ stacking between parallel rows of geometrically convergent aryl rings. The electronegative fluorine atoms, efficiently shielded from the polar lamellae, are segregated into the regions between adjacent layers and form short F···F interlayer contacts about crystallographic centres of inversion.

Key words: Sulfonamides, Layer Structures, Hydrogen Bonding, Halogen Bonding, $\pi\cdots\pi$ Stacking