Low-temperature X-ray structures of the following di(4-X-benzenesulfonyl)amines, HN(SO₂-C₆H₄-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), X = Me (3, orthorhombic, Pnca, Z'=1), X = Br (4A, monoclinic, P2₁/c, Z'=1), X = Br (4B, monoclinic, P2₁/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 N-H⋯O₁ in 1, 4A and 4B or N-H⋯O₂ 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 C-F⋯O/N contacts, but close F⋯F contacts are tolerated, whereas in 2 each catemer is connected to four parallel congeners by long and bifurcated C-Cl⋯O₂ bonds, and both polymorphs of 4 display layers in which the molecules are connected by N-H⋯O bonds in one and by relatively short and approximately linear C-Br⋯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 N-H⋯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 C-H⋯O and C-H⋯C(π) bonding. All the structures are pervaded by weak C-ar-H⋯O hydrogen bonds; moreover, 1 displays a short C-H⋯F hydrogen bond and a C-F⋯C(π) interaction, and π-stacking of aromatic rings is observed in 1, 3 and 4B.

Key words: Hydrogen Bonding, Halogen Bonding, π⋯π Stacking, C-H/C-F⋯C(π) Interactions, Sulfonamides