The effects of substitution were investigated for the sulfonamides class of molecules, in particular those which contain the benzosulfonamide functional group. This group of molecules is of extreme interest in the biological field since many of them are active against a variety of diseases. In this work, structural investigations on the pharmacophoric group benzosulfonamide and the substitution effects have been performed through the studies of its derivatives benzosulfonamide itself, para-toluensulfonamide, ortho-toluensulfonamide and the bioactive molecule sulfanilamide. In all compounds, but in ortho-toluensulfonamide, the amino group lies perpendicular to the benzene plane with the amminic hydrogens eclipsing the oxygen atoms. In ortho-toluensulfonamide where a weak attractive interaction between the nitrogen lone pair and the methyl hydrogen atoms takes place, the amino group lies in the gauche orientation. These results show that such weak non-covalent interactions are able to change the conformational preferences of the pharmacophoric group. For all species, the $^{14}$N quadrupolar hyperfine analysis has been performed. This has provided crucial information for the unambiguous identification of the observed conformation and the structural parameters related to the position of the nitrogen atom. In addition, for ortho-toluensulfonamide, the vibration-rotation hyperfine structure related to the methyl torsion has been analyzed and the methyl group rotation barrier was determined.