

Summary

The number of experimental charge density studies increased during the past years. This is prior to technical developments, especially the now widely spread area detectors which allow to measure high resolution X-ray diffraction data sets in a reasonable time. With the program system XD a computer program is available which enables the user to easily handle the substantial parameters in the Hansen-Coppens multipole formalism. The combination of the area detection technique with the highly intense primary beam intensity from synchrotron sources opens the method to more and more applications from all areas in chemistry.

In this work three different aspects of the method were investigated. The charge density study on thioproline yielded improved parameters for the radial expansion of the aspherical valence term of sulfur. Besides phosphorus and chlorine, sulfur is considered to be the most troublesome element in multipole refinements due to its diffuse charge distribution. Therefore a systematic study using two experimental diffraction data sets at 15 K and 120 K and theoretical structure factors from quantum chemical calculations was performed. The bond topological parameters of the sulfur-carbon bonds are compared to those from the studies on two penicillin derivatives and to results from literature. Although the radial parameters improve the multipolar description of sulfur some uncertainties remain.

In the charge density of two penicillin derivatives, the active penamecillin and the inactive penamecillin-1 β -sulfoxide, experience from the model compound thioproline could be used. Single crystals of both compounds were measured at the synchrotron beamline F1 at HASYLAB/DESY at 100 K. The cleavage of the amide bond in the β -lactam ring is of paramount importance in the mechanism of action of penicillins. The topological analysis shows that the strength of this bond is equal in both compounds. Therefore an influence of this parameter on the mechanism can be excluded. Based on the experimental electrostatic potential an explanation of the different antibacterial activity of the two compounds is proposed.

The fullerene derivative dodekakis-(ethoxycarbonyl)-C₆₀ is currently with more than 100 atoms in the asymmetric unit the largest molecule a charge density study with subsequent topological analysis has been performed on so far. The study represents a challenge on the method from an experimental and theoretical point of view. The topological analysis yields a correlation between the value of the electron density at the bond critical point which is a measure for the bond strength and the length of carbon-carbon bonds. Based on that correlation the strength of other carbon-carbon bonds can be predicted.