

Summary

Through the development of area detectors and the possibility of using intensive synchrotron radiation comparable charge density studies of entire classes of chemically related compounds can be accomplished[72][73]. The investigated substance can thereby increase (up to 100 atoms in the asymmetric unit or more). The limiting factor of the charge density analyses of even larger compounds is not the measuring time or constant measuring conditions during the measurement period but the insufficient crystal quality. To describe the electron density of those compounds the transferability of electronic and atomic properties is vitally important.

Matta presented a method, based on theoretical calculations, of reconstructing larger molecules from submolecular fragments. This concept was taken and applied to the morphine molecule. The atomic properties obtained experimentally were compared to the theoretical values of Matta and to those of new theoretical calculations of fragment molecules. The values of the theoretical calculated fragments fit very good to the values of Matta while the comparison of the atomic properties between experiment and theory shows some differences. The deviations cancel each other if CH_2 and CH_3 are regard as entire groups because the differences are caused by the slightly polarized C–H bond found in the experiment.

A further aspect of this work is the comparative charge density study of morphine and morphine related compounds. In this context six members of the class of opioids were determined from X-ray diffraction measurements. The experiments were carried out at very low temperature whereas three of these measurements were accomplished with the use of synchrotron radiation. The experimental charge densities were determined using the aspherical-atom multipole formalism according to Hansen and Coppens. The topological analysis of the electron distribution were applied according to Bader's theory of atoms in molecules (AIM). To compare these results theoretical charge densities were calculated at the density functional theory level of theory. In all cases a good agreement is found between the experimental and theoretical received topological parameters. The comparison between the experimental charge densities of the several compounds shows a very good congruity for chemical for those parts of the molecule having the same chemical environment, while differences in the chemical environment can be detected and visualized.

In addition to the bond topological properties the atomic properties were compared. They were defined by Bader's AIM theory and can be obtained by integration. The determination of the atomic properties represents a high computational requirement

and was used by default for molecules of this size for the first time. The very good accordance of the atomic properties confirms the theoretically predicted transferability of chemically similar atoms, functional groups or fragments[74][75][76]. The deviations can be explained by differences in the chemical environment. The comparison of the atomic properties and the electrostatic potentials between the neutral and protonated naltrexone derivative shows the distribution of the positive formal charge of the nitrogen atom over a large part of the molecule.

The characterization of the electronic structure of a halogenated fullerene derivative $C_{60}Cl_{30}$ represents a challenge due to the chlorine atoms which were problematic for the charge density analysis. It succeeded to measure in this work with conventional MoK_{α} radiation a high-resolution data set at 20 K.

The fullerene derivative is strongly distorted compared to the free C_{60} and contains a series of C–C bonds of different bond length which were topologically examined and compared with the results of theoretical calculations on HF and DFT level. The results of the experiment lie exactly between the two theoretical methods. The investigation of the extremely long C–C bond (1.70Å) in the fullerene cage shows a bent character, which is usually found in ring systems with large hoop stress. This bond can split by oxygen under formation of a ether bridge. For the C–C bonds the bond orders according to Bader were intended with consideration of the charge density at the bond critical point. Bond orders around $n=2$ are found for short bonds and bond orders distinctly smaller than 1 for long bonds. The degradation of the molecule symmetry by the deformation leads to the abolition of the equivalence of the carbon atoms in the C_{60} cage, which could be quantified on the basis the atomic volumes.