

KN23

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Ab-initio structure solution by automated electron diffraction tomography (ADT)

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Electron diffraction has been successfully used for structure solution of nano crystalline materials since fifty years. Nevertheless, there is still a strong need for a robust and less time consuming method providing three-dimensional electron diffraction data suitable to perform routine structure solution within kinematical approaches (intensities proportional to F_{hkl}^2). The core idea of Automated electron Diffraction Tomography (ADT), a recently developed approach for electron diffraction data acquisition and analysis [1, 2], is to collect off-zone diffraction patterns in a tilt sequence around an arbitrary axis with fixed tilt steps. Thus, dynamical effects are strongly reduced when compared with the traditional acquisition approach where in-zone patterns are collected. In addition, depending on the tilt step chosen, most of the reciprocal space can be scanned inside the microscope goniometer tilt range. The resulting off-zone diffraction patterns cannot be analysed manually, thus a dedicated software (ADT3D) was developed to reconstruct the three-dimensional reciprocal space. From this volume accurate cell parameters and orientation matrix are determined using clustering-routines, reflections are indexed and intensities integrated. The extracted 3D diffraction data is suitable for ab-initio structure solution by common X-ray diffraction program packages. Additionally, visual inspection of the reconstructed reciprocal space volume allows to detect crystallographic specialities such as superstructures, disorder, twinning or contributions from other crystals.

With the improved quantity and quality of ADT data sets ab-initio structure solution is already possible. Further improvement can be achieved by coupling ADT with precession electron diffraction (PED) [3], thus providing a more complete reflection integration throughout the missing wedge between the slices.

Based on ADT and ADT/PED data it was possible to solve about 30 structures in the last two years, some originating from single nanocrystals down to 30 nm [4]. Suitable data sets could be even derived from disordered [5] or agglomerated samples. Large cell porous minerals [6], zeolites [7], beam-sensitive metal-organic frameworks [8] and organic structures [9] have been solved by direct methods as used in X-ray crystallography. ADT data can be collected using standard TEMs [10] therefore the method has a high potential to be spread to other electron microscopy labs.

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KN24

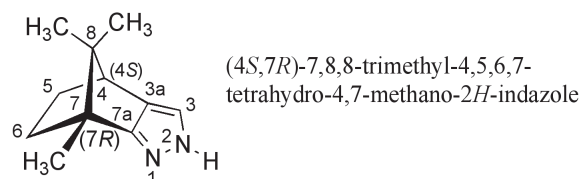
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Conflicts and complications between crystallography, solid state NMR and vibrational circular dichroism (VCD)

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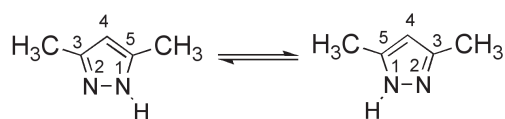
The structure of organic and organometallic molecules (including drugs) in the solid state cannot be determined only by crystallography if dynamic aspects are to be considered. The best approach is a combination of variable temperature (VT) cross-polarization magic-angle spinning (CPMAS) nuclear magnetic resonance (NMR) and theoretical calculations (geometries, energies, chemical shifts and spin-spin coupling constants). Today, CPMAS NMR is to crystallography of small molecules as very high-field solution NMR is to protein crystallography.

When single crystal determination is not possible and powder diffraction is difficult, NMR combined with *ab initio* or DFT calculations can be used to get knowledge about the structure of the compounds. A particularly interesting case is that of molecules with high Z' values, for instance, camphopyrazole ($Z' = 8$):

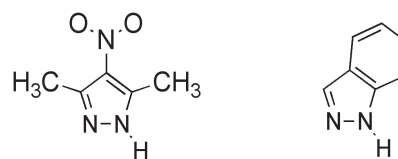


Since crystallography and NMR cannot be physically connected, a possible solution is to use hierarchical clustering trees.

Disorder in crystals can be static or dynamic and CPMAS DNMR (dynamic NMR) is the method of choice to decide. When the disorder is due to molecular motions (conformational or proton transfer), DNMR will provide with kinetic parameters such as activation energies. For instance, solid-state proton transfer occurs in 3,5-dimethylpyrazole between both nitrogen atoms:



There are some achiral molecules that crystallize forming conglomerates. This is the case of 3,5-dimethyl-4-nitropyrazole and indazole; both crystallize forming helices and in each single crystal only one class of helix (either *P* or *M*) is found. The use of solid-state VCD (vibrational circular dichroism) together with theoretical calculations allows to determine the absolute configuration and to count the number of crystals of each parity.



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