

Chemical Shifts and Crystal Structure of Methylnitroacetanilide

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Two polymorphic forms („white“ and „yellow“) of methylnitroacetanilide (MNA) have been studied by magic-angle spinning (MAS) NMR and by computations of shielding. The ^{13}C spectra of the two forms are very different and show (in conformity with known crystal structures) that the crystallographic asymmetric units are one and two molecules respectively. The differences in chemical shifts are explained by computation in terms of the dihedral angles the two side-chains make with the aromatic ring. High-speed MAS proton spectra reveal high-frequency resonances which are assigned to hydrogen-bonded protons. However, shielding computations show that these shifts are not consistent with the supposed positions of the protons for the white form of MNA. Computations produce a plot of shielding vs. N-H distance from which the N-H bond length can be accurately determined to be 1.033 Å.

This method of obtaining interatomic distances, i.e. of using NMR shifts together with computations on the molecule of interest only, is new. We have validated it by applying it to the case of L-histidine hydrochloride hydrate. In this case the method gives results at variance both with the structure determined from X-ray diffraction and with NMR measurements of dipolar coupling constants, but it gives good agreement with data from neutron diffraction.