Poster Presentation

MS35.P33

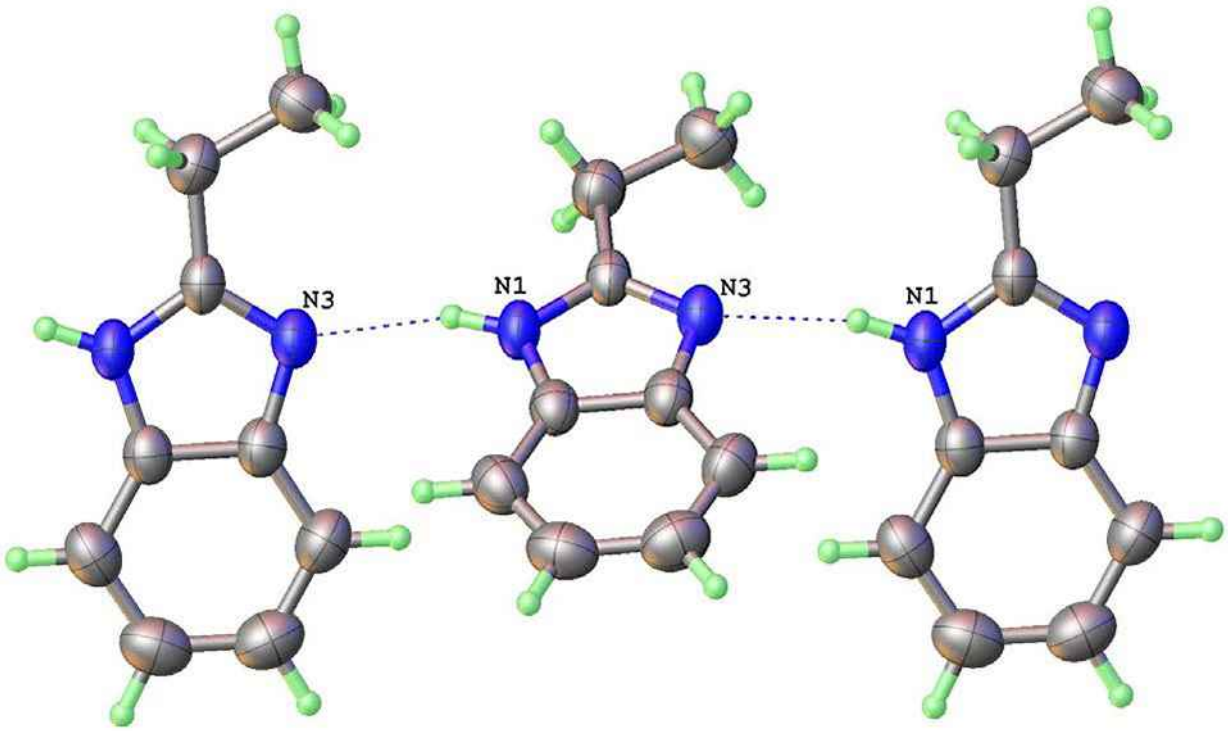
Studies of NH--N Hydrogen Bond Chains in Imidazoles by Neutron Diffraction

I. Williams[1], Y. Zhou[1], Y. Zhang[1], H. Sung[1], A. Edwards[2]

[1]HKUST, Department of Chemistry Clear Water Bay, Hong Kong, [2]ANSTO, Bragg Institute, Lucas Heights, Australia

Crystals of imidazole compounds typically organize themselves with NH---N hydrogen bonded 1D chains in the absence of other hydrogen bond donor or acceptor groups. The 'synthon' is robust, but can vary considerably in length, which is related to the pKa and the linearity of the hydrogen bond. For symmetric imidazoles with effectively perfect pKa matching of the two N atoms, this implies that many crystals may exhibit statistical disorder of the hydrogen positions. However X-ray studies alone cannot readily distinguish the true extent of this, since unlike carboxylic acid analogues, even fully ordered systems show little difference in the N(1)-C(2) and N(3)=C(2) bond lengths of the imidazole ring. Despite their fundamental nature, surprisingly few neutron studies have been carried out on such NH---N systems and only the parent compound imidazole itself has been examined in depth.[1,2] Herein we report the extension of this to a range of other imidazoles and benzimidazoles. In particular 2-methylbenzimidazole [3] and 2-ethylbenzimidazole are ideal candidates to allow study of bent and linear, ordered and disordered hydrogen bond chains in this family of compounds. Neutron data were collected at low temperature on these and other compounds, using specimens of around cubic 1mm on KOALA Laue neutron diffractometer at the Bragg Institute, Australia. The results support the general findings of related single crystal X-ray studies. However the N-H positions are obtained with good accuracy and correlations of covalent N-H to intermolecular H--N can be made. They also confirm that essentially full ordering of hydrogen bond chains in crystals such as 2-Ethylbenzimidazole (shown in Figure) is possible, with only a single 'negative peak' for the proton position found along the N---N vector. This may have positive implications for the development of such crystals as molecular ferroelectrics. The authors are grateful for an award of beam-time by ANSTO (Proposal 2765).

[1] *B. M. Craven, R. K. McMullan, J. D. Bell, et al., Acta Crystallographica, Section B, (1977), 33, 2585,* ***[2]*** *R. K. McMullan, J. Epstein, J. R. Ruble, et al., Acta Crystallographica, Section B, (1979), 35, 688,* ***[3]*** *A. E. Obodovskaya, Z. A. Starikova, S. N. Belous, et al., J. Struct. Chem. (1991), 32, 421-2*



Keywords: Hydrogen Bonds, Neutron Diffraction, Crystal Engineering