

Synchrotron and neutron diffraction structural study of 4-methylpyridine-N-oxide at low temperature

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The interpretation of non-linear dynamics arising from the collective rotation of methyl groups in molecular compounds requires an accurate knowledge of the compound crystal structure at low temperature, in order to provide realistic modelling of the effective potentials experienced by the methyl rotors. Molecular compounds generally exhibit complex structures with large unit cells ($> 2000 \text{ \AA}^3$), and even though neutron diffraction experiments are mandatory to locate reliably the hydrogen atoms in the structure, they often need to be coupled with high resolution synchrotron data. A good example is the way the 10K structure of 4-methylpyridine-N-oxide was recently solved. This molecular compound exhibits three structural phases : above 139K, the tetragonal unit cell ($I4_1/amd$) contains 8 equivalent molecules oriented along the c axis. At $91\text{K} < T < 139\text{K}$, the cell is orthorhombic ($Fddd$), and the 16 equivalent molecules are rotated by about 8° around the c axis with respect to positions at high temperature. To solve the low temperature phase ($T < 91\text{K}$), cell parameters were first determined from synchrotron powder diffraction data at 25K. A simulated annealing process using clusters of integrated intensities extracted from the synchrotron diffraction data was then run to determine the positions and orientations of the eight independent molecules in the unit cell ($P4_1$, $a = b = 15.410(2)\text{\AA}$ and $c = 19.680(3)\text{\AA}$, $Z = 32$). This result was subsequently used in the refinement of a neutron powder diffraction pattern collected at 10K on a deuterated sample in order to locate precisely the deuterium atoms. Results evidence that, though at 250K and 100K the deuterated methyl groups are largely (dynamically) disordered, at 10K they are ordered in phase along infinite chains parallel to a and b . Face-to-face methyl groups along c are in an eclipsed configuration. The structure at 10K suggests that the manifold of rotational tunnelling transitions observed in inelastic neutron scattering could be due to inequivalent lattice sites for methyl groups.