LOW TEMPERATURE STRUCTURE OF THE N-OXY γ-PICOLINE BY USING SIMULATED ANNEALING ON NEUTRON AND SYNCHROTRON POWDER DIFFRACTION DATA

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The study of the rotation dynamics of methyl groups is of paramount importance to understand the phase transitions that undergo methylated compounds in the solid state. It is supposed that the non-linear excitations generated by the methyl dynamics (*breathers* and *rotobreathers*) [1,2] play a fundamental role in the biological functions of aminoacids and proteins. To tackle the study of the methyl dynamics it is necessary to know the crystal structure at different temperatures of the concerned model compounds. In this document we present the case of the 4-methyl N-oxy pyridine (N-oxy γ-picoline, $C_5H_4NO[CH_3]$, hereafter NOPic) that presents two structural phase transitions below room temperature (RT). These transitions generate modifications in the distribution density of the methyl groups in a way similar to that observed in 4-methyl pyridine [2]. The structure of NOPic at RT ($I4_1/amd$, a=7.943(3), c=19.621(5) Å) has Z=8 molecules in

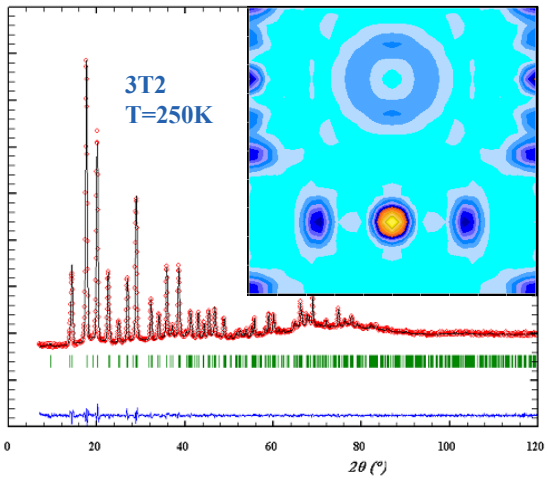

Figure 1. Refinement of the RT phase of NOPic and Fourier map of a section containing methyl groups. Notice the nearly circular proton density.

the unit cell and shows a complete disorder of the methyl groups. The CH_3 groups are rotating, around the axis of the molecule, giving rise to a quasi-circular distribution of proton density (Fig. 1) [2, 3]. Below T_2= 138 K the structure becomes orthorhombic (*Fddd*, a=12.140(1), b=10.239(1), c=19.573(1) Å, Z=16) and the planes of the molecules become tilted (rotation around the **c**-axis) with respect to the RT phase. The methyl groups are still disordered and the proton density distribution is modified slightly (Fig. 2). A new

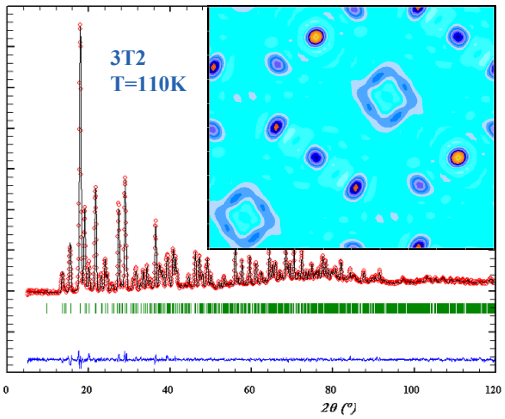

Figure 2. Refinement of the intermediate phase of NOPic and Fourier map of a section containing methyl groups.

phase transition is observed at T_1=91K, as can be seen in the portions of neutron diffraction patterns presented in Figure 3 showing the three kinds of diffraction patterns observed for NOPic. The structure of the low temperature phase was not known before this work. The study using single crystals has been up to now hampered by the strong twinning observed in the *Fddd* phase that, on the other hand, was refined using neutron powder diffraction. We have used the LLB high-resolution powder diffractometers G4.2 (λ=2.38 y 3.13 Å) and 3T2 (λ=1.23 Å), using a deuterated sample to eliminate the incoherent scattering of protons, to get the appropriate structural information. However, we were not able to succeed in indexing the Bragg peaks of the low temperature (LT) phase using neutrons. The unit cell of the LT phase was the unknown before performing the experiments in the Swiss-Norwegian Beam Line (SNBL, λ=0.689 Å) at the ESRF. Thanks to the very good resolution of the powder diffractometer in the SNBL and the use of indexing programs distributed within the *FullProf Suite* [5] we got the LT unit cell that turns out to

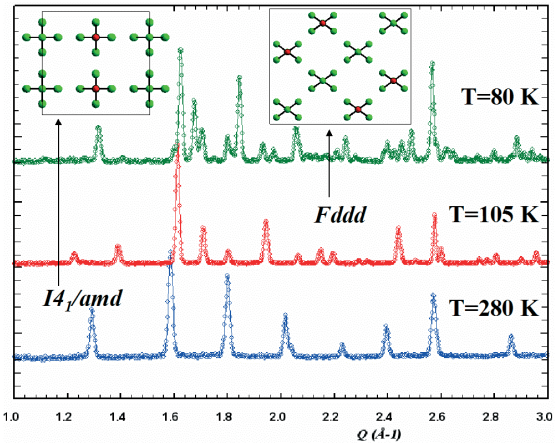

Figure 3. Limited portions of the neutron diffraction patterns of the N-oxy γ-picoline. Schematic structure of the two previously known structures as seen from [001]. Hydrogen atoms are not represented.

be tetragonal (a=15.943(3), c=19.621(5) Å, Z=32). So, there is a sequence of phase transitions on cooling where the tetragonal symmetry of the RT phase is partially recovered in the LT phase ($a_{LT} \approx 2\times a_{RT}$, $c_{LT} \approx c_{RT}$). The possible space groups where studied starting with those of higher symmetry compatible with the molecular distribution in the RT phase. The resolution of the structure was performed by the Simulated Annealing option implemented in FullProf [5], using clusters of overlapped integrated intensities. The space group finally found is $P4_1$, in which there are Z/4=8 independent NOPic molecules. The success of the resolution critically depends on the use of rigid body modelling parameters, the number of free parameters (6 per rigid block) used in the resolution of the structure was 6× Z/4 = 48, and a proper election of their variation limits. It is interesting to notice that the data from long wavelengths neutrons of G4.2 (λ=3.13 Å) are as good as those of synchrotron for solving the structure. The asymmetric unit has 120 atoms and preliminary refinements, with the Rietveld method, using the 3T2 data has confirmed that the phase transition takes place by shifting the centres of the molecules and making small tilts of the molecular planes that remain otherwise nearly parallel to the **c**-axis like at the other temperatures. The methyl groups seem to be well localized but with an unexpected configuration. It is interesting to realise that the LT phase has mixed characteristics of the two higher temperature phases (Fig.4).

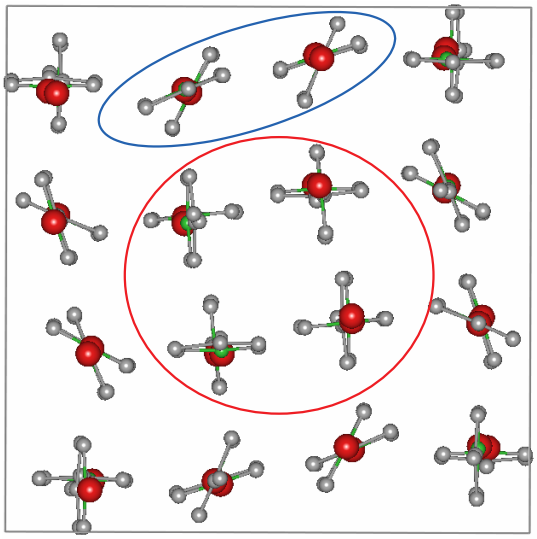

Figure 4. View along [001] of the NOPic structure in its LT phase as obtained from simulated annealing. There are parts of the structure roughly similar to the high temperature (red ellipse) and to the intermediate phase (blue ellipse). The hydrogen atoms are not shown.

References

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