Experimental report

18/09/2017

Proposal:	**5-12-325**	**Council:**	4/2016
Title:	Order-disorder transition of a triazoyl ketone		
Research area:	Materials		

This proposal is a new proposal

Main proposer:	**Valerie DUPRAY**
Experimental team:	Morgane SANSELME Valerie DUPRAY
Local contacts:	Estelle MOSSOU

Samples: $C_{15}H_{18}Cl_1N_3O$

Instrument	Requested days	Allocated days	From	To
D19	10	10	29/09/2016	10/10/2016

Abstract:

A family of organic compounds exhibits an order-disorder transition of its t-butyl group that can be monitored by TR-SHG (Temperature Resolved Second Harmonic Generation). Solid State NMR experiments indicate that for temperatures lower than the temperature of order/disorder of the carbon of the t-butyl, the 1H NMR peaks attributed to these hydrogen atoms become broader. This can be interpreted as the possible non equivalence of the hydrogen atoms at the molecular level. In this context, this phenomenon could be due to the freezing of the motion of the hydrogen atoms. However, it seems difficult from these data to clearly describe the behavior of the hydrogen atoms of the t-butyl upon cooling. Neutron diffraction experiments should allow us to accurately locate the hydrogen atoms at various temperatures and therefore to determine the sequence of the freezing steps for this molecule.

Report of Research proposal 75243

The goal of this study was to determine the freezing sequence upon cooling of the t-butyl group of a compound belonging to a family of triazole ketones labeled X-TAK (X=H, Me, Et, Cl), and more precisely of the Cl-TAK (Fig.1).

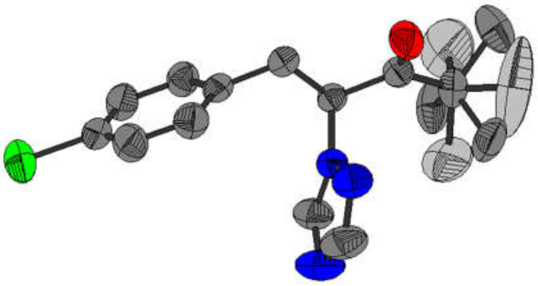


Figure 1: Ortep plot for Cl-TAK, showing the methyl carbon site occupancy factor (sof = 78/22), in light/dark grey for the minor/major conformation. For clarity the hydrogen atoms were omitted

Some previous studies (Temperature resolved X-ray diffraction on single crystal) have shown that the t-butyl group is disordered on two limit positions with a minor and a major sof. And as temperature decreases the sof value diminishes and tends to reach a steady state where the t-butyl becomes "frozen". This phenomenon was observed between 253K and 233K (the recording temperature in X-ray diffraction). Furthermore, some SHG analyses emphasized a structural modification occurring at 243K (Fig 2). NMR analyses were performed below this frozen temperature (at 213K) with the aim of checking the existence of a possible motion of the Hydrogen atoms. Results exhibited some ambiguous behavior for the motion of the Hydrogen atoms of the t-butyl group, i.e. as if these atoms were not equivalent.

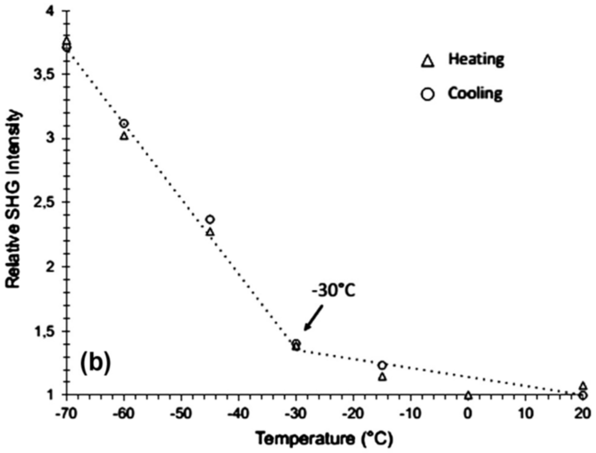


Figure 2: Disruption in the intensity values of Temperature resolved SHG measurement, for Cl-TAK at -30°C (243K).

In order to clarify these results, Neutron Diffraction experiments were performed at ILL. The Neutron diffraction experiments were performed on the Cl-TAK compound (Fig 1), at various temperatures (20, 295, 250, 220, 200, 180, and 220 K). The measured statistical occupancy factors (sof) were determined and values are summarized in table 1.

Table 1: Statistical occupancy factors vs temperature

Temperature (K) (in the order of the performed measurements)	**Statistical occupancy factor** (extracted from Neutron diffraction data)
20 K	100%
295 K	82%
250 K	87%
220 K	93% (all) / 93% (first scan cut)
200 K	95% (all data) / 100% (first scan cut)
180 K	100%
220 K	94% (all) / 100% (first scan cut)

Results show that the frozen temperature extracted from the Neutron data does not fit with the results of the previous X-Ray studies (Figure 3).

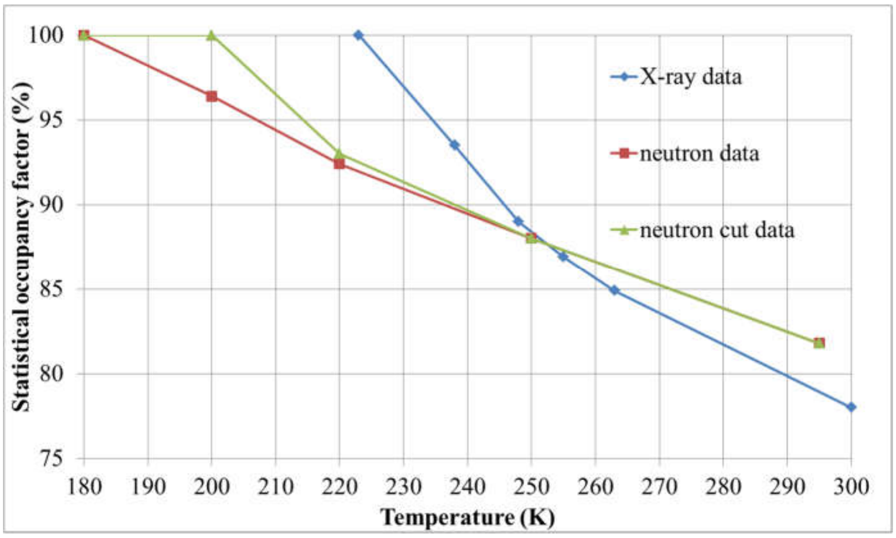
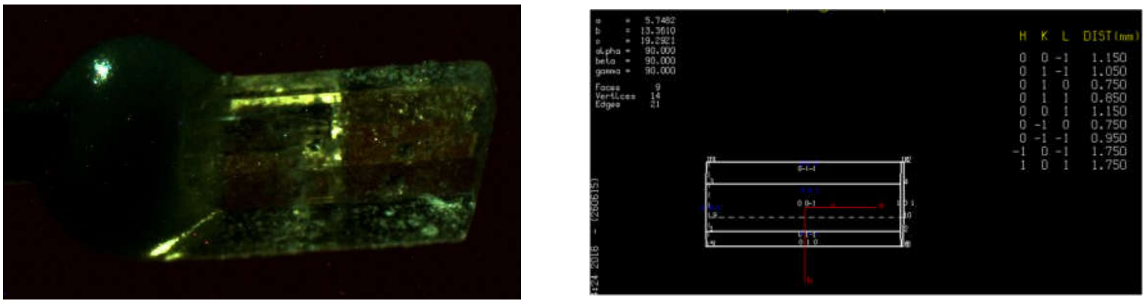


Figure 3: Statistical occupancy factors (sof) vs Temperature from X-ray diffraction data (blue), from neutron diffraction data (red) and from cut neutron diffraction data (green) (see table1).

Compared to X-Ray data (which gave a freezing temperature between 233 and 253K), the freezing temperature of t-butyl extracted from neutrons data is shifted toward lower values (below 200K).

A reason envisaged for these discrepancies was a thermal inertia of the crystal upon cooling and/or heating (ie. if the crystal is too big for the cold beam and the flux doesn't cover all the crystal, it takes larger time to ensure the freezing of the conformation). Thus, the set temperature could be different from the effective temperature of the crystal for the first neutron scans. To take this possibility into account, the first scan for 200K and 220K (second recording) were excluded from the calculation. This led to a slightly higher freezing temperature extracted from neutron data (upper than 200K – see fig. 3). However, this is not sufficient to compensate the deviations observed.

Indeed, if the freezing temperature observed in X-ray and suggested by SHG measurements (circa 253 K) is correct, at 220K upon heating from a frozen state, the molecule should remain ordered and a 100% sof should be obtained from Neutron data (ie. once the conformation is frozen, and if upon heating the crystal remains at a temperature below the one corresponding to the appearance of the disorder, then the conformation should remain blocked).


a = 5.7482
b = 13.3610
c = 19.2921
alpha = 90.000
beta = 90.000
gamma = 90.000

Faces 9
Vertices 14
Edges 21

H	K	L	DIST (mm)
0	0	-1	1.150
0	1	-1	1.050
0	1	0	0.750
0	1	1	0.850
0	0	1	1.150
0	-1	0	0.750
0	-1	-1	0.950
-1	0	-1	1.750
1	0	1	1.750

Figure 4: Photography and indexation of the crystal analyzed by neutron diffraction

Nevertheless, Neutron data better fit with RMN results that seem to indicate a freezing temperature below 220 K. Therefore, the structural modification observed in SHG could be due to another phenomenon such as a variation in the speed rate of the motion of the disordered conformation or a modification of the polarizability of the molecule (due to the variation of the sof). However, this hypothesis fells to explain the good match of the temperatures observed by SHG and X-ray data (for all the tested compounds).

Some data modelling is currently in progress to calculate the polarizability of the Cl-TAK at various sof in partnership with CRIANN (Centre Régional Informatique et d'Applications Numériques de Normandie). Beyond that, it is important to consider that the motion observed is statistical and that the speed rate between the two limit conformations is not known. This speed rate may be the key factor that allows to understand the different data obtained so far.