

# Structure and dynamics of the crystalline stable phase of 2-chlorothiophene

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## Abstract

The dynamics of a simple and rigid molecule (2-chlorothiophene) has been studied by means of broadband dielectric spectroscopy (BDS) within the low-temperature stable crystalline phase, whose structure has been determined by means of X-ray powder diffraction (XRPD) measurements. The triclinic  $P1$  structure consists of two molecules per asymmetric unit ( $Z'=2$ ) with site occupancies 80:20 and 60:40 for each molecule of the asymmetric unit. Such a statistical intrinsic disorder is associated with two dynamical relaxation processes corresponding respectively to out-of-plane relaxations around the C-Cl two-fold molecular axis and in-plane reorientational motions as proposed previously (Fujiromi and Oguni, *J. Phys. Chem. Solids* **1993**, *54*, 437-612). The XRPD and BDS measurements allow rationalizing published nuclear quadrupole resonance data. We show that only the concurrent use of different experimental techniques provides the answer to a complicate case of orientational molecular dynamics in the solid state.

## Introduction

Structural glasses are obtained by cooling or pressurizing liquids, which are ergodic disordered systems with both translational and orientational disorder.<sup>1-3</sup> The dynamics of the system slows down fast enough to avoid the transition to a more ordered state, generally the fully ordered crystalline state. When the ergodic state is translationally ordered but orientationally disordered (as in a plastic crystal or a rotator phase), the reorientational motions of the molecules can be also frozen in the same way, giving rise also to a glassy state called orientational glass and exhibiting the same dynamic features and thermodynamic anomalies.<sup>4-12</sup> As far as dynamic processes are concerned, in addition to the omnipresent cooperative  $\alpha$  relaxation (ascribed in structural glasses to their viscous flow), also secondary relaxations with shorter relaxation times appear, which may have different origins.<sup>6,13-19</sup> Among them, the Johari-Goldstein  $\beta$  relaxation process exhibited even by rigid molecules is quite common and can be interpreted on the basis of the energy-landscape picture as jumps between the basins<sup>20,21</sup> within a metabasin and generally follows the predictions of the Coupling Model<sup>22-24</sup> The existence of dynamic processes has been made evident even for highly ordered systems such as translationally ordered phases with an intrinsic statistical disorder involving only the site occupancy of one or few atoms of the (rigid or flexible) molecular entities.<sup>9-12,25-29</sup> In these cases, the distinct site occupancy probabilities (called fractional occupancies) reflect the existence of perfectly defined, discrete allowed angular orientations of the molecules which undergo reorientational jumps between the allowed orientations, in contrast to the undefined and hardly quantifiable dynamics of translationally and orientationally disordered phases such as the liquid state. The study of these minimally disordered crystalline systems with few and quantifiable disordered configurations can allow the precise identification of the different dynamic processes observed experimentally, as well as on the required minimal disorder for the emergence of the so-called universal thermal anomalies of the glass state. Here we report on the low-temperature crystalline phase of 2-chlorothiophene ( $C_4H_3ClS$ ), a derivative of the five-membered sulfur heterocyclic thiophene ( $C_4H_4S$ ) molecule. Thiophene is a very simple and rigid molecule which displays a rich polymorphism, with five stable and three metastable crystalline phases, for which large amplitude in-plane molecular reorientations have been reported.<sup>30,31</sup> The easiness of the reorientational motions was attributed to the molecular shape (similar to a short cylinder) and to the van der Waals interactions, both allowing rotations between distinct discrete orientations around the quasi five-fold axis perpendicular to the molecular plane within the

herringbone structure of the different polymorphs.<sup>30</sup> This “simple” system is very sensitive to subtle changes of the intermolecular interactions, as proven by the reported effect of isotopic substitution of H by deuterium: in the low-temperature crystal phase of C<sub>4</sub>D<sub>4</sub>S (phase V, stable below 112 K), the molecules are perfectly ordered, unlike the low-temperature phase of C<sub>4</sub>H<sub>4</sub>S which is disordered with a reported glassy transition temperature at 42 K.<sup>32</sup> It was speculated that the in-plane reorientational motion in the hydrogenated compound is prevented in the deuterated compound due to the larger molecular mass, and thus a larger moment of inertia. Solid methane (CH<sub>4</sub>) is another example of a system where subtle changes in the disorder are caused by isotopic effects.<sup>33</sup> The 2-chlorothiophene derivative was first studied by means of adiabatic calorimetry within the range of 13 and 300 K<sup>34</sup> and few years later by nuclear quadrupole resonance (NQR) from 200 K down to 77 K.<sup>35</sup> Calorimetric measurements revealed two thermal anomalies in the crystalline phase (melting temperature of 201.3 K) at 164 and 186 K. From the calorimetric measurements, the authors proposed the existence of two different kinds of motions, namely five-fold rotations (of  $2\pi/5$  angular amplitude) around an axis perpendicular to the molecular plane, and two-fold out-of-plane ( $\pi$ ) rotations about the C-Cl molecular axis. In terms of the crystalline structure detectable in XRD measurements, the occurrence of in-plane rotations would imply fractional occupancy probabilities for both the chlorine and sulfur atoms, while the out-of-plane rotations would lead only to a disorder of the sulfur atom within the asymmetric unit cell (assuming that such a rotation keeps the molecular plane invariant). The NQR study pointed out the existence of two broad (100 kHz full width at half maximum) <sup>35</sup>Cl signals with almost identical temperature variation in the measured temperature range. Although this was not acknowledged by the authors of the NQR study, the detection of two distinct <sup>35</sup>Cl NQR signals actually reveals the existence of two independent chlorine atoms within the asymmetric unit of the crystal. The temperature variation of the spin-lattice relaxation time ( $T_1$ ) was accounted for assuming two dynamic processes, namely the typical libration modes active also at low-temperature ( $T_1 \propto T^n$ , with  $n \approx 3.1$ ), and an activated process ( $T_1 \propto e^{-E/RT}$ ) with an activation energy of 53 kJ·mol<sup>-1</sup>. The lack of information about the crystal structure prevented a rationalization of the physical origin of the NQR data as well as a compatibility check to discard or support the existence of the proposed molecular motions.

In this work we determine experimentally the crystal structure and dielectric relaxation dynamics of the low-temperature phase of 2-chlorothiophene, and reanalyze the NQR data with these new pieces of evidence. We demonstrate that the out-of-plane rotations are accompanied by a small change of the molecular plane, in particular, by a change of the orientation of the C-Cl bond. The in-plane rotations proposed early by Fujimori and Oguni<sup>34</sup> can only appear as short-lived molecular fluctuations undetectable by X-ray diffraction; they must therefore involve at least one non-equilibrium configuration as it was recently found in some haloethane compounds.<sup>25,36</sup> These results allow a microscopic identification of both the primary and secondary dielectric relaxation processes that we observe experimentally.

### **Materials and Methods**

2-Chloro-thiophene (C<sub>4</sub>H<sub>3</sub>ClS, M<sub>w</sub> = 118.58 g/mol) was purchased from Sigma-Aldrich with a purity higher than 96% and used as provided.

Differential scanning calorimetry (DSC) experiments were carried out in both high-pressure stainless-steel and aluminum pans under nitrogen atmosphere, by means of a DSC-7 calorimeter from Perkin-Elmer. Measurements were performed in the temperature range from 170 K to room temperature, with a heating/cooling rate of 2 K/min and masses around 10 mg.

High resolution X-ray diffraction patterns were recorded at room temperature with a cylindrical position-sensitive detectors (CPS120) from INEL (France) using monochromatic Cu-K $\alpha_1$  ( $\lambda = 1.54061$  Å) radiation. The generator power was set to 40 kV and 25 mA. X-ray patterns on a liquid sample sealed in a 0.3-mm diameter Lindemann capillary, which were rotated around their axes during data collection to improve averaging of the crystallites, were obtained as a function of temperature (from 90 K to the melting point) by means of a 600 series cryostream cooler from Oxford Cryosystems.

External calibration was performed by means of cubic phase Na<sub>2</sub>Ca<sub>3</sub>Al<sub>2</sub>F<sub>4</sub> mixed with silver behenate. The peak positions were determined by pseudo-Voigt fittings.

The acquisition times were of at least 7h for the structural determinations at low-temperature and 30 min for pattern matching procedure to determine the variation of the lattice as a function of temperature. Indexing of the X-ray powder diffraction patterns,

structure solutions, and Pawley and Rietveld refinements were performed using Materials Studio Program.<sup>37</sup>

Broadband dielectric spectroscopy (BDS) measurements were carried out using a Novocontrol Alpha analyzer. The liquid sample was placed in a stainless steel parallel-plate capacitor specially designed for the analysis of liquid samples, with the two electrodes kept at fixed distance by means of silica spacers of 50  $\mu\text{m}$  diameter. Temperature control was achieved with a nitrogen-gas flow cryostat (Quatro) with an error not higher than 0.3 K. Measurements were done in the frequency ( $\nu$ ) range between  $10^{-2}$  and  $10^6$  Hz.

Relaxation time values were obtained by fitting the dielectric loss spectra with a power law for the conductivity contribution and a superposition of Cole-Cole (CC) functions for the relaxation peaks. The analytical expression of the CC function is:

$$\varepsilon^*(\omega) = \varepsilon' - i\varepsilon'' = \varepsilon_\infty + \frac{\Delta\varepsilon}{1+(i\omega\tau)^c} \quad (1)$$

where  $\varepsilon_\infty$  is the permittivity in the high frequency limit,  $\Delta\varepsilon$  is the dielectric strength,  $\omega$  is the circular frequency ( $\omega = 2\pi\nu$ ),  $c$  is the width parameter ( $0 \leq c < 1$ ) describing the shape of the loss curves and  $\tau$  is the characteristic relaxation time. The fit functions used to model the relaxation processes were actually of the more general Havriliak-Negami type, whose spectral line shape is asymmetric and depends on a second exponent, but the free fits gave a better agreement with the experimental data when such exponent was equal to one, corresponding to the Cole-Cole case.

## Results

DSC measurements (see Figure S1 in Supporting Information) revealed only the occurrence of the melting of the crystalline phase at  $200.4 \pm 1.0$  K with a transition enthalpy of  $\Delta H_{\text{S} \rightarrow \text{L}} = 9.2 \pm 0.5$  kJ mol<sup>-1</sup>, virtually the same values as those reported by Fujimori and Oguni<sup>34</sup> from adiabatic calorimetry (201.3 K and 8.966 kJ mol<sup>-1</sup>), who employed an extra-pure compound for their measurements.

The X-ray diffraction patterns of the solid phase were indexed by means of the X-Cell software available in the Powder Indexing of Materials Studio modeling software, using a long-time acquisition pattern measured at 160 K. The indexing procedure yielded a triclinic structure with  $Z=2$  according to a reasonable molecular density. The lack of systematic absences is compatible with two different space groups, namely the enantiomorphic  $P1$  and the centrosymmetric  $P\bar{1}$ . NQR experiments<sup>35</sup> (see later) and Rietveld refinement provided a compatible solution with the  $P1$  space group with  $Z=2$ . A Pawley refinement was performed using the initially determined lattice parameters in space group  $P1$  and they were refined together with zero-point shift, background, peak-profile (under pseudo-Voigt function) and peak asymmetry parameters.

For structural determination, a rigid-body molecule was built up through the Forcite software (also available in the Materials Studio package). Molecular bond distances and angles were, within the available accuracy, in agreement with previously published data for the molecule in the gas phase obtained from electron diffraction.<sup>38</sup> With such a rigid-body constraint, two molecules of the asymmetric unit ( $Z'=2$ ), as inferred from the two signals obtained from the NQR experiments, were put in the cell and the structure was solved through the Powder Solve module including March-Dollase function as preferred orientations.<sup>39</sup>

The final Rietveld refinement provided the position and orientation of both molecules in the unit cell.

As for the thiophene case, the results indicate that the two independent molecules display a statistical disorder. Several models were then analyzed. A first model was built up assuming that both molecules were perfectly ordered, a hypothesis which is however in disagreement with the dielectric spectroscopy results and NQR data (see later). A second model was based on two disordered molecules for which the respective S atoms can occupy two different sites related by a two-fold rotation around the C-Cl molecular axis (assuming that Cl atoms occupy the same position). Although this model provided reasonable refinement factors, it did not provide the right solution that should contain a disorder related to the Cl atom, as discussed in the introduction.

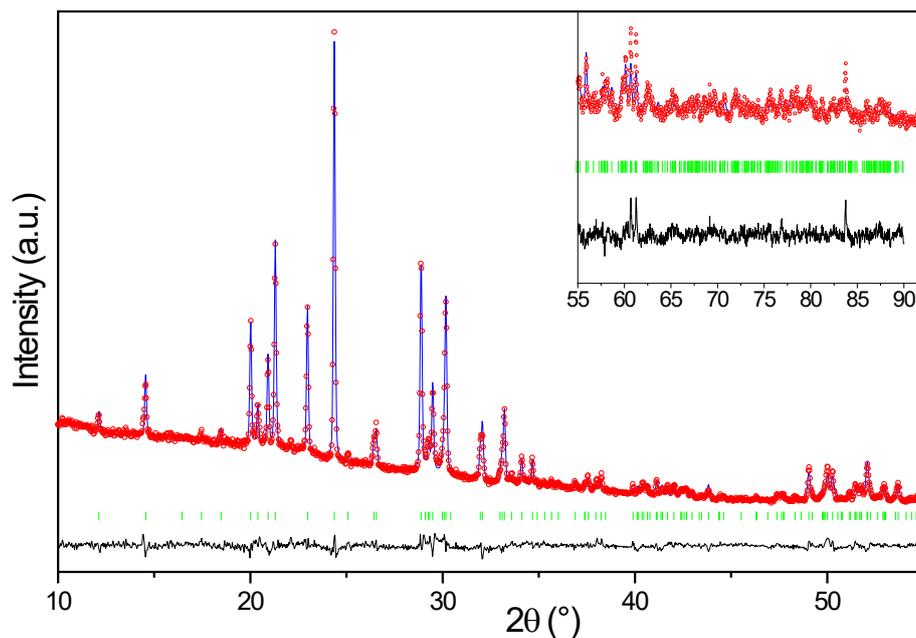
The best solution compatible with the spectroscopic NQR results, was based on two molecules having each a different orientation and different occupancy factors. For one of the molecules (molecule M1) in the asymmetric unit, the occupancy factors at 160 K turned out to be 60:40, whereas for the other one (molecule M2) the ratio is found to be 80:20. It should be especially emphasized that for both molecules both the S and Cl atoms

(which are largely responsible for the molecular dipole moment) are disordered between two sites, in such a way that the C-Cl angle difference between each occupied site for molecule M1 is around  $2.4^\circ$  whereas for molecule M2 it is  $6^\circ$  (see CIF file for the fractional coordinates at 160 K).

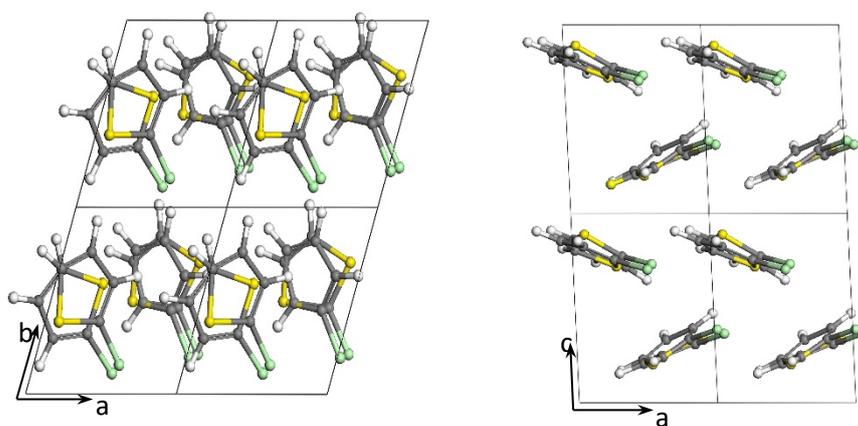
The refinement results based on this model are depicted in Figure 1, in which the calculated profile is shown together with the experimental pattern, their mutual difference, and the Bragg reflections. Final refined parameters are collected in Table S1 of the Supporting Information. Figure 2 shows two projections of the *P1* triclinic phase of 2-Cl-thiophene at 160 K refined structure (along *c* and along *b* planes)

In order to determine the temperature-dependence of the lattice parameters the liquid sample was cooled relatively fast to 90 K and X-ray diffraction patterns were subsequently acquired on heating every 10 K till 160 K and afterwards every 5 or 3 K till the melting temperature. The results are plotted in Figure 3 for lattice parameters (Figures 3A-F) as well as for the molar volume (Figure 3G). It can be observed that lattice parameters show a kink at ca. 180 K, without a change in the overall structure.

Figure 3H displays the difference in C-Cl angle between the two possible molecular orientations for both molecules (1 and 2) of the asymmetric unit, as determined from Rietveld refinements at each temperature. It can be observed that the angular difference for molecule 2 reveals a noticeable change in the temperature dependence above 190 K, in such a way that the difference between the two molecular orientations increases at high temperature, i.e., the reorientational jumps of the C-Cl bond take place between more distant positions.



**Figure 1.** Experimental (red circles) and calculated (blue line) X-ray diffraction patterns along with the difference profile (black line) and Bragg reflections (vertical green sticks) for the final Rietveld refinement of the *P1* triclinic phase of 2-Cl-thiophene at 160 K.



**Figure 2.** Projection of the refined structure of the *P1* triclinic phase of 2-Cl-thiophene at 160 K along *c* (left) and along *b* planes (right). Color of the atoms: Cl green, S yellow, C gray, H white.



(at lower frequency) corresponds to the cooperative primary  $\alpha$  relaxation, as detailed below. Each loss component was fitted as the imaginary part of a CC function (eq. 1) so as to obtain the characteristic relaxation times for the slow and fast relaxations,  $\tau_\alpha$  and  $\tau_\beta$ , respectively. Figure 4B plots the relaxation times for both processes, which are observed to follow a simply activated Arrhenius behavior ( $\tau = \tau_0 e^{E/RT}$ ) with activation energies  $E_\alpha = 82.3 \pm 0.7 \text{ kJ mol}^{-1}$  and  $E_\beta = 72.4 \pm 0.7 \text{ kJ mol}^{-1}$ , respectively. The identification of the slower  $\alpha$  process as the primary relaxation follows from the fact that the dynamic glassy transition temperature obtained by our BDS data, defined as the temperature at which the relaxation time  $\tau_\alpha$  reaches 100 s, is 164 K, which is virtually the same temperature  $T_{g1}$  found from adiabatic calorimetry.<sup>34</sup> This would imply that the statistical disorder observed in our XRPD data is dynamic above 164 K, and largely static below this temperature, where the  $\alpha$  process is kinetically frozen.

Our assignment of the  $\alpha$  relaxation is also confirmed by our analysis of the NQR data, as we discuss in the following. It is interesting to point out that the strength of the  $\alpha$  relaxation increases with increasing temperature, especially above approximately 180 K (see the inset to Figure 4A). This is consistent with our XRPD results, since at this temperature the initial and final molecular orientations after the out-of-plane start differing by larger and larger angles, which entails a larger change in the electric dipole moment of the molecules upon reorientation and thus a larger contribution to the dielectric loss and static dielectric constant.

The interpretation of the secondary  $\beta$  relaxation is less straightforward. The fact that the  $\alpha$  and  $\beta$  relaxations do not merge at high temperature, and the fact that the so-called Coupling Model<sup>22-24</sup> does not allow to predict the relaxation time of the secondary relaxation from the spectral parameters of the primary relaxation, indicate that the  $\beta$  relaxation is not of the Johari-Goldstein type. Its lower strength (lower effective dipole moment density) indicates that it might correspond to a small-angle reorientational motion, which could perhaps correspond to small angle ratcheting librations of the molecule which leave almost invariant the position of the sulphur atom (no out-of-plane rotation), while changing the position of the chlorine between the two possible crystallographic positions at each site.

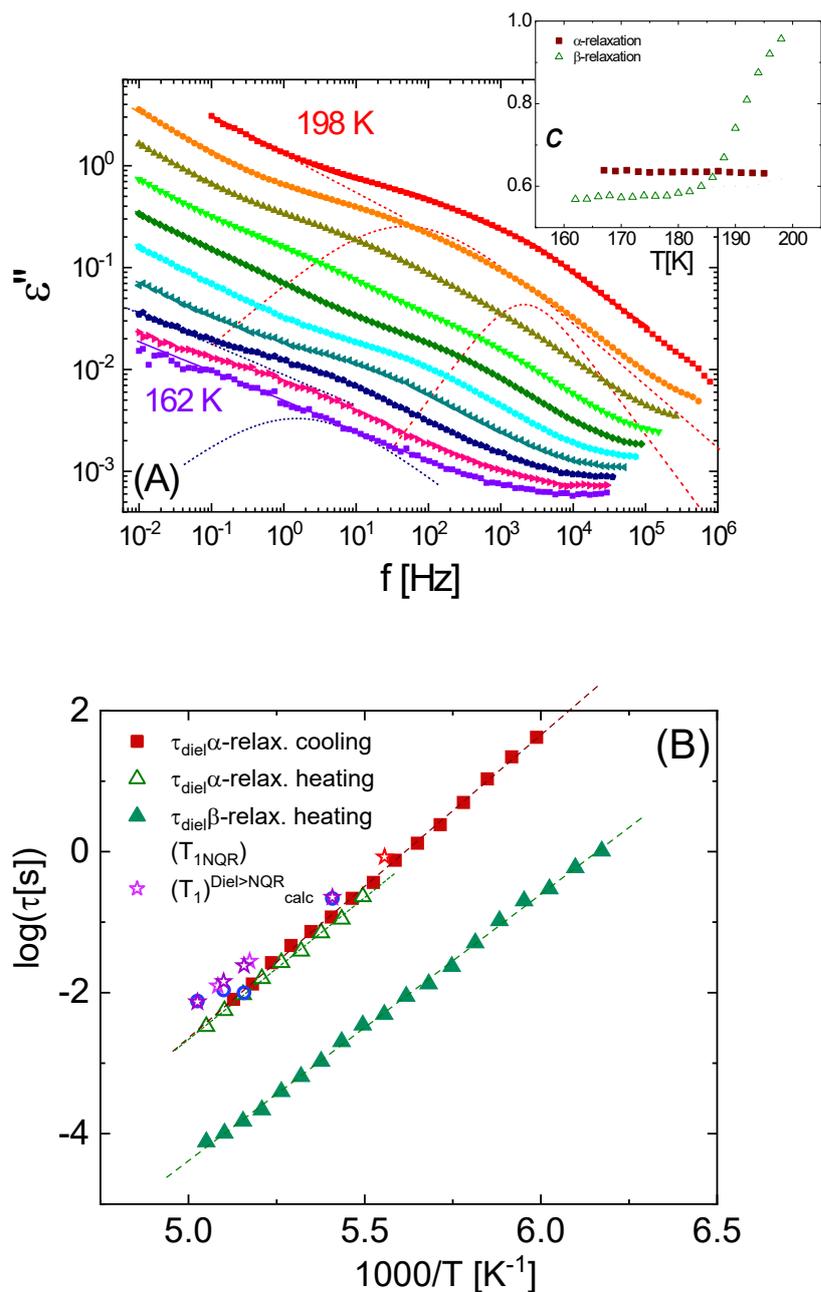


Figure 4. (A) Loss spectra of the stable triclinic phase of 2-Cl-thiophene measured between 162 and 198 K, every 4 K. Continuous lines are the fits of the spectra at each temperature, dashed red lines are the fits of conductivity contribution and the slow ( $\alpha$ ) and fast ( $\beta$ ) relaxations for the spectrum at 198 K. Blue dashed lines are the conductivity and  $\beta$  relaxation contributions at 170 K. Inset: Cole-Cole width parameter  $c$  ( $0 \leq c < 1$ ) describing the shape of the  $\alpha$  and  $\beta$  loss curves as a function of temperature. (B) Arrhenius plot of the slow relaxation  $\tau_{\alpha}$  (filled red squares) and fast  $\tau_{\beta}$  (filled green triangles) relaxation times, obtained from the loss dielectric spectra displayed in panel (A).

Continuous lines are the fits according to the Arrhenius law. Blue circles are NQR spin-lattice relaxation times minus the lattice vibration contribution ( $\Delta T_1$ ) and pink stars are the values of  $\Delta T_1$  generated with eq. 4 at the same temperatures.

## Discussion

As mentioned, our structural analysis has shown the existence of two molecules in the asymmetric unit (and also in the unit cell,  $Z=Z'=2$ ) with temperature independent occupancies of 60:40 and 80:20 for molecules labeled as 1 and 2, respectively. For this herringbone structure, the disorder can be interpreted as resulting from an out-of-plane rotation of each molecule around its pseudo-2-fold molecular axis, which is accompanied by a small tilt of the C-Cl bond direction (both molecules are not in the same plane before and after the out-of-plane reorientation).

To account for such a disorder, the angle between C-Cl bonds between the two occupied sites for each molecule was determined. In other words, the molecular dipole of molecules 1 and 2 of the asymmetric unit can reorient between two different orientations being discernible by the  $\phi_1$  and  $\phi_2$  represented in Figure 3H. This figure reveals that not only the fractional occupancies are different for molecules 1 and 2, but also slightly the angle between the molecular sites. According to these structural evidences and the emergence of two relaxation processes in the loss dielectric spectra, the two dynamical processes should be ascribed to out-of-plane molecular reorientations between different sites, giving rise to the main slow and cooperative  $\alpha$  relaxation, and small angle dipole reorientations due to localized molecular librations ( $\beta$  relaxation).

In order to confirm the origin of the slow  $\alpha$  relaxation and provide more insight on that of the fast  $\beta$  relaxation, published NQR experiments<sup>35</sup> were reanalyzed in the light of the structural results from this work.

The temperature dependence of <sup>35</sup>Cl NQR frequency and spin-lattice relaxation time ( $T_1$ ) were measured in the 77-200 K range.<sup>35</sup> The reported NQR spectrum consists in two broad peaks with a full width of about 100 kHz at half maximum each, which is an indication of crystal disorder. This broadening arises from random strains, electric fields, and other perturbations from the “defects” in the lattice containing the nuclei whose transitions are studied.<sup>40</sup> The NQR spectra at 77 K, reproduced in Figure 5A, and the fit

with two Gaussian functions shows that the area ratio between low and high frequency peaks is 2. As the unit cell consists of two independent molecules, two peaks of the same intensity are expected a priori, and not a ratio of 2:1. This ratio can however be understood if we consider that the two molecular orientations have different occupation factors. Using statistical methods it is possible to reproduce these inhomogeneous lineshapes according to the distribution, density and perturbation fields of individual defects<sup>40,41</sup>, in ionic crystals<sup>42</sup> or molecular crystals<sup>43</sup>. The last model not only reproduces broadening of the NQR lines but the appearance of satellite lines due to the discreteness of the lattice,<sup>43-45</sup> and since it was successfully applied in halogenated benzenes and their molecular alloys.<sup>46</sup>

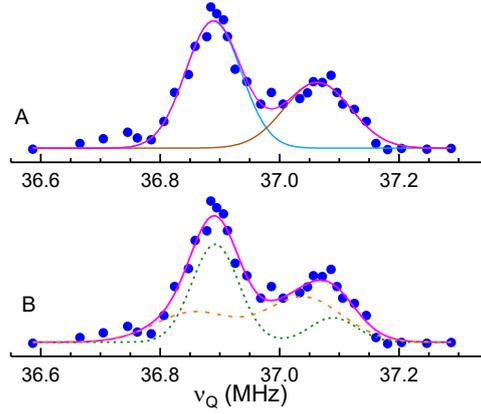
For each quadrupolar nuclei in a non-equivalent site the NQR line width can be accounted by the distribution<sup>43</sup>

$$g(\nu) = \frac{1}{\sqrt{2\pi}\sigma} \left( C_{c1} e^{-\frac{(\nu - \bar{\nu} - \nu_{c1,1})^2}{2\sigma^2}} + C_{c2} e^{-\frac{(\nu - \bar{\nu} - \nu_{c2,1})^2}{2\sigma^2}} \right) \quad (2)$$

Where  $C_{c1}$  and  $C_{c2}$  are the proportions or occupational factors of molecules with configuration  $c1$  or  $c2$  (the two positions between which the molecule reorientates),  $\nu_{c1,1}$  and  $\nu_{c2,1}$  are the change of the Cl NQR frequency due to changes in its first neighbor,  $\sigma^2 = C_{c1}C_{c2}\sigma_o^2$ ,  $\bar{\nu} = C_{c1}\nu_1 + C_{c2}\nu_2$ , are the width and the mean frequency, respectively, that depend on the occupation factors and  $\sigma_o$ ,  $\nu_1$  and  $\nu_2$  the differences in NQR due to the two orientations of the molecules.

Due to the existence of two non-equivalent Cl atoms in the asymmetric unit, the NQR line must be fitted according to two distributions, as represented by eq. (2), one for each of the non-equivalent Cl atoms. According to the fractional occupancies of 60:40 and 80:20 for molecules 1 and 2, respectively, factoring parameters in eq.(2) were settled as  $C_{c1}= 0.6$  and  $C_{c2} = 0.4$  and  $C_{c1}= 0.8$  and  $C_{c2} = 0.2$ , for the Cl lines of molecules 1 and 2, respectively.

The excellent fit in Figure 5B shows that the split is similar for the two Cl atoms belonging to the inequivalent molecules in the cell,  $\Delta\nu = \nu_{c1,1} - \nu_{c2,1} > 160$  kHz, and the broadening  $\sigma$  is 40 and 60 kHz for each contribution. These splitting and broadening values are similar to those found in orientationally disordered halobenzenes.<sup>43</sup>



**Figure 5.** NQR line shape from ref 35. (A) Fit of NQR line with two Gaussians with an intensity ratio 2:1. (B) Fit with the distribution given in eq. (2). Dashed line  $g(\nu)$  for the Chlorine with occupation 60:40, dotted line  $g(\nu)$  for Chlorine with fractional occupation 80:20.

According to the results from Fujimori and Asaji<sup>35</sup>, at low-temperature the  $^{35}\text{Cl}$  spin lattice relaxation time  $T_1$  has a normal behavior due exclusively to torsional oscillations or lattice vibrations  $(T_1)_{\text{lib}}$ <sup>46,47</sup> while above 180 K another relaxation mechanism, following an Arrhenius behavior, appears. When molecular reorientations take place and quadrupole nucleus belongs to the reorienting group,  $(T_1)_{\text{reo}}$  is proportional to the jump correlation time.<sup>48,49</sup> When the nuclei do not jump but the electric field gradient (EFG) of the observed nuclei is modulated by reorientations of molecules or molecular groups a contribution,  $(T_1)_{\text{mod}}$ , appears.<sup>47</sup>

Then, the temperature dependence of  $T_1$  in molecular crystals can be usually expressed as the superposition of different contributions due to lattice vibrations  $(T_1)_{\text{ph}}$ , slow reorientations of the quadrupolar atom,  $(T_1)_{\text{reor}}$ , and reorientations of Cl neighbors groups,  $(T_1)_{\text{mod}}$ :

$$\frac{1}{T_1} = \left(\frac{1}{T_1}\right)_{\text{ph}} + \left(\frac{1}{T_1}\right)_{\text{reor}} + \left(\frac{1}{T_1}\right)_{\text{mod}} = AT^\lambda + \frac{k(\theta)}{\tau_{\text{reor}}} + \frac{1}{6} \left(\frac{q'}{q}\right)^2 \frac{\omega_q^2 \tau_{\text{reo}}}{1 + \omega_q^2 \tau_{\text{mod}}^2} \quad (3)$$

The exponent  $\lambda$  for the lattice vibrational contribution is found to be between 2 and 3, but usually closer to 2.  $\tau_{\text{reor}}$  is the jump correlation time,  $k(\theta)$  is a factor that depends on the geometry of the reorientation and  $(q'/q)$  denotes the ratio between the fraction of the

electric EFG affected by the molecular reorientation and the total EFG in the Cl site. For slow reorientations ( $\omega_Q \cdot \tau \gg 1$ ) the modulation term is also proportional to  $\tau_{mod}$ , but because in molecular crystals  $(q'/q) < 0.05$ <sup>50</sup> its contribution is smaller by a factor  $6(q'/q)^2 \sim 10^4$ .

To have a reliable description of the disorder and the associated dynamics, we will use the information of dielectric results as well as the structural obtained details to reproduce the relaxation data in NQR.

In order to determine the molecular reorientational dynamics we subtracted the lattice vibrational contribution  $(T_1)_{ph}$ , from the low-temperature range, to the  $T_1$  experimental data. Then, within the slow reorientation regime we will have:

$$\frac{1}{T_1} - \left(\frac{1}{T_1}\right)_{ph} = \Delta T_1^{-1} = \frac{k(\theta)}{\tau_{reor}} + \frac{1}{6} \left(\frac{q'}{q}\right)^2 \frac{1}{\tau_{mod}} \quad (4)$$

We use the dielectric relaxation times  $\tau_\alpha$  and  $\tau_\beta$  in eq. (4) to reproduce  $\Delta T_1^{-1}$  values matching  $\tau_{reor}$  and  $\tau_{mod}$  with some of the times  $\tau_\alpha$  and  $\tau_\beta$ , respectively. Within this hypothesis, two consequences can be derived: (i) Due to the change of the neighbor molecular charges (S atom), there would be a contribution to the relaxation (modulation) which can be accounted with the factor  $6(q'/q)^2 (< 0.01)$ . The only possibility that this process contributes to the observed values of  $\Delta T_1^{-1}$  is that it occurs with the shortest relaxation time  $\tau_\beta$  and with  $(q'/q) = 0.03$ . (ii) For reorientational jumps that involves the Cl atom,  $k(\theta) = 3/2(1 - \cos^2(\theta))$ <sup>48</sup> or  $k(\theta) = (1 - (3\cos^2\theta - 1)^2/4)$ <sup>49</sup> depending if the Cl atom jumps between two equivalent or non-equivalent potential wells with  $\theta$  being the angle that the C-Cl bond rotates. If Cl atom remains at the same position, there is no contribution ( $\theta=0$ ,  $k(\theta)=0$ ). Although X-ray structural solution does not support the in-plane jump reorientation we can try to see the contribution to NQR of this movement. In this case  $\theta$  will be  $72^\circ$  giving a  $k(\theta)$  factor of 1.5, that would imply that the generated  $\Delta T_1^{-1}$ , with the eq. (4), values will be below the experimental ones if we use  $\tau_\alpha$  and even smaller with  $\tau_\beta$ . Therefore this reorientation is clearly discarded. But from the structural results, it is found that not only the S atoms are disordered but also the Cl with a small angle of rotation changing from  $4^\circ$  at low temperature to ca.  $10^\circ$  near the melting point. By assuming  $\theta = 10^\circ$  with  $\tau_\alpha$ , we have a value of  $\Delta T_1^{-1}$  close to the experimental one.

In Figure 4B the different relaxation times are shown: Long  $\tau_\alpha$  and short  $\tau_\beta$  relaxation times obtained from dielectric measurements, reorientational relaxation time  $\Delta T_1^{-1}$  derived from NQR and  $\Delta T_1^{-1}$  according to eq.

$$\Delta T_1^{-1} = \frac{k(10^0)}{\tau_\alpha} + \frac{1}{6}(0.030)^2 \frac{1}{\tau_\beta} \quad (5)$$

that is, introducing the dielectric relaxation times in the eq. (4).

Thus, NQR data are compatible with two different movements conducting to the disorder determined from X-ray diffraction and with the characteristic times found from dielectric spectroscopy: out-of-plane slow relaxations around the C-Cl two-fold molecular axis and small angle fast reorientations of the C-Cl bond.

The change of the C-Cl bond jumps giving rise to the  $\beta$  relaxation as demonstrated by the NQR analysis produces a noticeable change in the thermal expansion at around 185 K, as revealed in Figure 3G (which is mainly due to the temperature variation of the lattice parameter  $a$ , see Figure 3A). Moreover, this change is accompanied by a change in the relaxation time distribution, as indicated in the temperature variation of the  $c$  parameter of the CC equation (see inset in Figure 4A). This parameter decreases fast from high-temperature, close to the melting point, down to ca. 185 K, reaching a value of 0.58. The broadening of the  $\beta$ -relaxation peaks can be ascribed to the existence of heterogeneity of the dynamics of the system, which leads to a wider distribution of relaxation times. It gives rise also to a change in the dielectric strength of the  $\beta$  relaxation (not shown). Such a widening (see inset in Figure 4A) is related to and goes with a slowing down of the thermal expansion of the lattice. It should be emphasized that as for the C-Cl jumps originating the  $\beta$ -relaxation, the two molecules in the asymmetric unit do not contribute in the same way, as revealed by the angle of the jumps (see Figure 3H). Whereas one molecule (molecule 2) changes the angular amplitude of the jumps at ca. 185 K on increasing temperature, molecule 1 keeps the slow increase with temperature without a noticeable change. This experimental fact contributes to prove the heterogeneity of this relaxation. As for the  $c$  parameter of the  $\alpha$ -relaxation (out-of-plane molecular reorientations) as a function of temperature, it can be observed that does not feel the

change in the lattice expansion and thus the cooperativity of this process remains the same till the glass transition temperature (164 K).

In the light on these results, the specific heat anomaly reported by Fujimori and Oguni<sup>34</sup> at 164 K is clearly associated with the freezing of the out-of-plane molecular reorientations, while the in-plane possible reorientations claimed from those authors are discarded. Consequently, the reported specific heat anomaly at 186 K,<sup>34</sup> cannot be originated by the in-plane reorientations. The authors fitted the relaxation enthalpy data around 186 K according to a stretched exponential and a value of  $\beta^{\text{KWW}}$  stretched exponent of 0.6 was obtained. They associated the low value of the exponent with a coupling between the two possible types of disorder, out-of-plane and in-plane, despite, as claimed from the authors, the glass transition temperature (164 K) for the slower process is relatively far away. According to our measurements, our  $\beta^{\text{KWW}}$  stretched exponent calculated<sup>51</sup> through the  $\beta^{\text{KWW}}=(c)^{1/1.23}$  is ca. 0.66, so virtually the same. Nevertheless, the  $\beta$ -relaxation cannot be attributed to the in-plane reorientational process because it is incompatible with the structure, but as demonstrated by NQR analyses and coherently ascribed from the BDS experiments, to the C-Cl jumps of one molecule of the asymmetric unit. Nevertheless, it should be noticed that in-plane reorientational process can appear as short-lived molecular fluctuations (not detectable by X-ray diffraction) between one equilibrium site and a non-equilibrium site, with a short residence time, as it was found for some haloethane compounds.<sup>25,26</sup>

## Conclusions

We have investigated the dynamics and the structure of the crystalline phase of 2-Cl-thiophene by means of broadband dielectric spectroscopy and X-ray powder diffraction. The stable crystalline phase of this compound displays a complex triclinic  $P1$  lattice structure, with two molecules per asymmetric unit with site occupancies 80:20 and 60:40 for each molecule. The occupational disorder is associated with the existence of a reorientational dynamics consisting of out-of-plane ( $\pi$ ) rotations around roughly the C-Cl bond, but such that the orientation of this bond is not the same before and after the out-of-plane reorientation. Such cooperative dynamics is responsible for the main dielectric

loss (slow  $\alpha$  relaxation), while the fast secondary  $\beta$  relaxation is associated to small angle librations that change the position of the Cl atoms while leaving virtually invariant that of the S atoms. The former relaxation is kinetically frozen ( $\tau=100$  s) at 164 K, which matches perfectly the glassy transition temperature early obtained from specific heat measurements.<sup>34</sup> As for the thermal effect reported by the same authors at ca. 186 K and initially attributed to the onset of large-angle rotations around an axis perpendicular to the molecular plane (of  $2\pi/5$  angular amplitude), which the authors of the previous studies referred to as in-plane rotations, lattice structure demonstrates that these rotations are discarded (at least between stable occupational sites). Moreover, it is demonstrated that such thermal effect is related to a sudden increase of the amplitude of the C-Cl angle between the two different occupational sites of one of the molecules in the asymmetric unit, an effect which is accompanied by a broadening in the relaxation time distribution of the fast  $\beta$ -relaxation.

The relaxation dynamics of the 2-Cl-thiophene molecule within the crystalline phase reported in the present study nicely explains the NQR measurements published in an earlier work.<sup>35</sup>

As a general conclusion, this work demonstrates how “simple systems” displaying a disorder limited to a low number of degrees of freedom can be used to elucidate the microscopic origin of the  $\alpha$ - and  $\beta$ -relaxations.

## **ASSOCIATED CONTENT**

### **Supporting Information**

Figure S1: DSC measurement for the melting process. Table S1: Crystal structure information and Materials Studio results of the Rietveld refinement for the 2-Cl-thiophene This information is available free of charge via the Internet at <http://pubs.acs.org/>.

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## Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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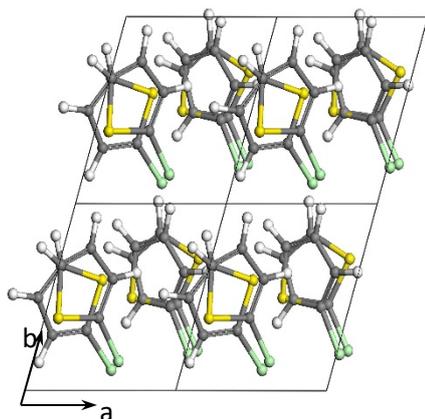
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**For Table of Contents Use Only:**

## Structure and dynamics of the crystalline stable phase of 2-chlorothiophene

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### Synopsis

The structure of the disordered triclinic structure of 2-Cl-thiophene has been determined by means of X-ray powder diffraction and the thermal anomalies previously reported as glass transitions have been identified through broadband dielectric spectroscopy and nuclear quadrupole resonance.