ESRF	**Experiment title:** Correlation of structural and electronic properties in the microcrystalline phases of the organic superconductor $(ET)_2I_3$	**Experiment number:** CH-478
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Report:

The organic superconductor $(ET)_2I_3$ has been produced by chemical oxidation which gives phase pure single-crystals in the micrometer size [l]. It turned out that the highest quality samples that were obtained were of the β form.

Several data sets were collected on β-$(ET)_2I_3$ at different temperatures. A high quality data set was collected at 200K to a resolution of 0.7Å on a crystal of dimensions 12x10x2μm. Averaging of -19000 reflections to 3960 unique showed a good internal agreement of the squared structure factors; R_{int}=0.036.

The structure was refined both in Pi, which is the space group found in the literature [2], and the acentric equivalent Pl. One of the ethylene groups is disordered, and the high quality of the data allowed a refinement of the populations of the two possible conformations of the disordered group. In Pi the populations show a 0.50(2) population for the two possible conformations. In Pl there are two ET molecules in the asymmetric unit and in one of the molecules the populations for the two conformations of the ethylene group are 0.43(5) and 0.57(5) while in the other they are 0.54(5) and 0.46(5).

In the crystallographic model the population of the I_3^- was refined and showed that the chemical oxidation of (ET) was almost complete with an I_3^- population of 0.981(2).

The refinement in Pi had a final R1=0.047 in SHELXL-97.

On the same crystal, a good data set was collected at 100K with an internal agreement of the squared structure factors (R_{int}) of 0.052 giving 3900 unique reflections. The resolution was the same as at 200K, 0.7Å and the multiplicity was -4. The crystal had suffered some damage. That was observed in the population of the I_3^- group, which had dropped to 0.931(3).
In the literature, a phase transition to an incommensurately modulated structure is reported at 175K [3], but we did not observe this in the phase pure single-crystals.
The structure was refined in both Pl and $P\bar{1}$ as for the data collected at 200K. The populations of the two possible conformations of the disordered ethylene group had changed to 0.40(5) and 0.60(5) for both cations in the asymmetric unit in the refinement in the space-group P1. In the refinement in space group $P\bar{1}$ the populations were 0.40(3) and 0.60(3), respectively. From these populations of the two possible conformations of the disordered ethylene group one can determine the energy difference between the two states (called P(1) and P(2)):

$$\frac{P(1)}{P(2)} = e^{-\Delta E/kT}$$

The energy difference is determined to 0.34kJ/mol at both temperatures. Extrapolating this argument to 30K gives P(1)=0.2 and P(2)=0.8. At the critical temperature, T,=7.8K, the populations would be P(1)<0.01 and P(2)>0.99 – the structure becomes ordered. This is with the assumption that there is no structural phase transition in the temperature interval from 100K to 7.8K which is uncertain.

It would be of fundamental interest to supplement the present two structures with at least two more data sets at low temperature to confirm that the driving force behind the superconducting properties is a disorder → order second order phase transition. These data sets would also show whether the phase transition at 175K reported in literature is an artifact of the electrochemically produced crystals used in previous studies.

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[2] H. Endes, H. J. Keller, R. Swietlik, D. Schweizer, K. Angermund, and C. Kruger, ***Z. Naturforsch.,*** **41a** (1986), 1319-1324.
[3] A. Nogami, S. Kagoshima, T. Sugano, and G. Saito, ***Synthetic Metals,*** **16** (1986), 367-377.