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Investigation of the Transient Modulated Phase of Barluenga's Reagent.

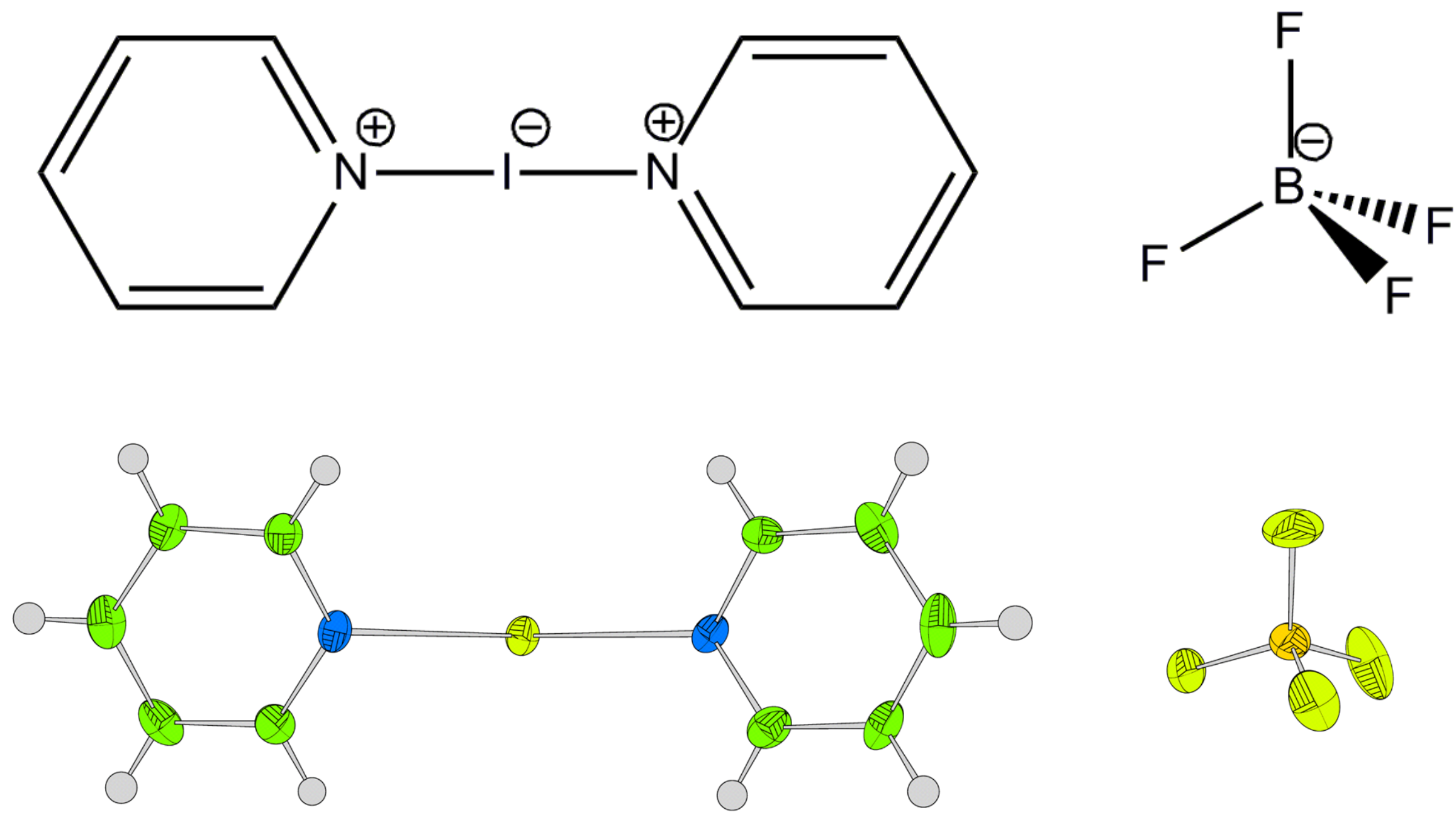
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Introduction

Bis(pyridine)iodonium(I) tetrafluoroborate,^[1] [IPy₂]⁺[BF₄]⁻ (also known as Barluenga's Reagent), is an iodinating and oxidising agent.



The reagent is known to have a solid state phase transition. Routine investigations were used to characterise the phase transition. Techniques employed included variable temperature Single crystal X-ray Diffraction and solid state NMR. During these investigations a transient modulated phase was observed.

Phase Transition

Unit cell parameters were collected over a range of temperatures and indicated that the transition occurred gradually over a range of temperatures around 200 K. The full data sets at 250(2) K and 150(2) K were solved and refined (using CRYSTALS)^[2] to give both the high and low temperature structures;

High Temperature

- Space Group C2/n,
- Only half the molecule in asymmetric unit,
- BF₄⁻ ion disordered around 2-fold rotation axis,
- Large ADPs indicate considerable movement of pyridine.

Low Temperature

- Space Group P2₁/n,
- One whole molecule and two half molecules in asymmetric unit,
- Two BF₄⁻ counter ions.

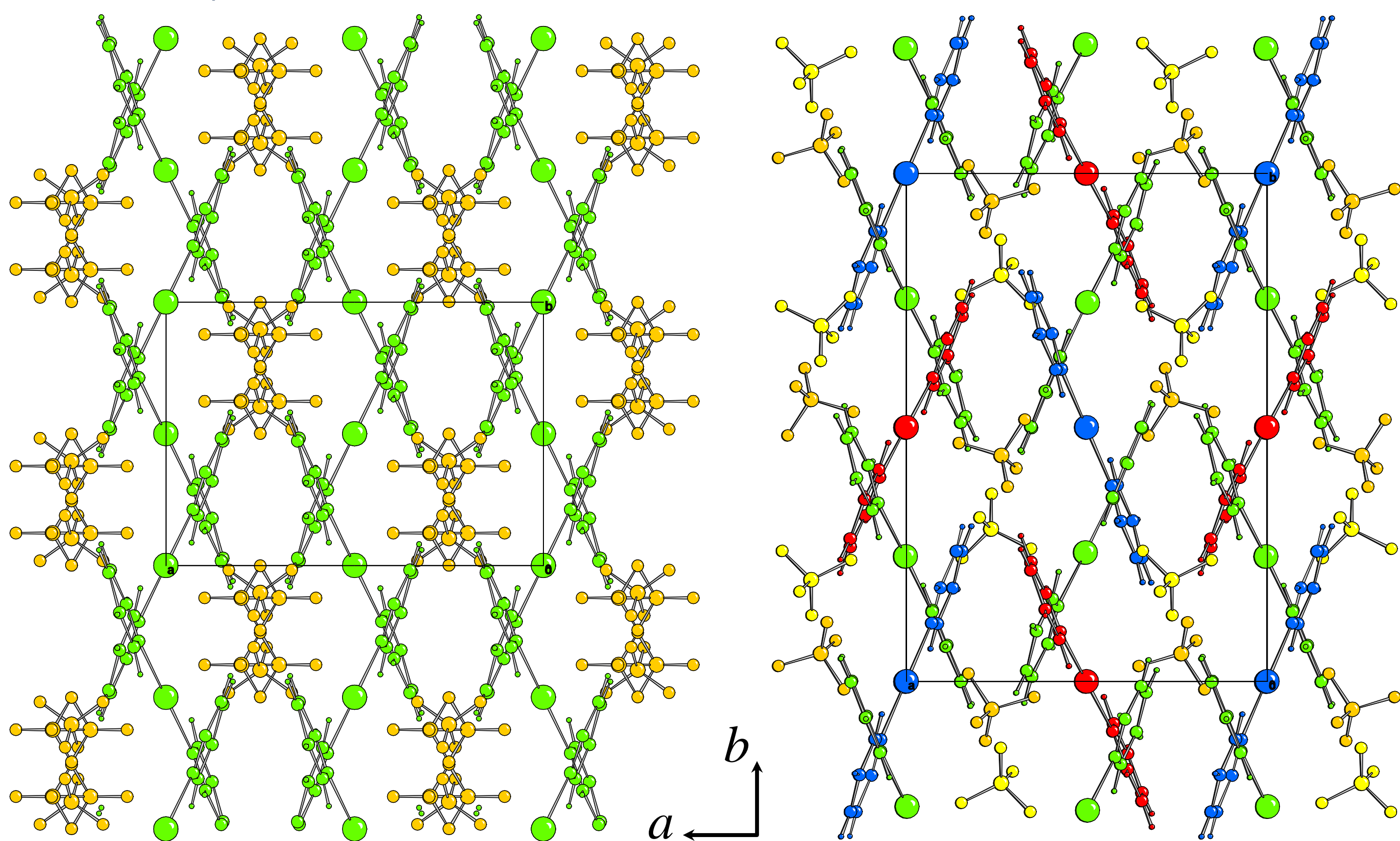


Figure 1 - The structure at 250 K (left) and at 150 K (right) viewed down the *c* axis. The IPy₂⁺ are shown in green, red and blue; the BF₄⁻ are shown in orange and yellow.

The main difference between the two structures is the loss of the two-fold rotor in the *b* direction, the *c* - glide perpendicular to *b* and the associated inversion centres. The loss of these inversion centres forces the cell to double resulting in the iodine moving to a general position.

Quantitative Analysis

Cell parameters and temperature factors were determined using the high temperature cell in the same orientation to enable the phase transition to be shown graphically. Both graphs below show a clear discontinuity around the transition temperature.

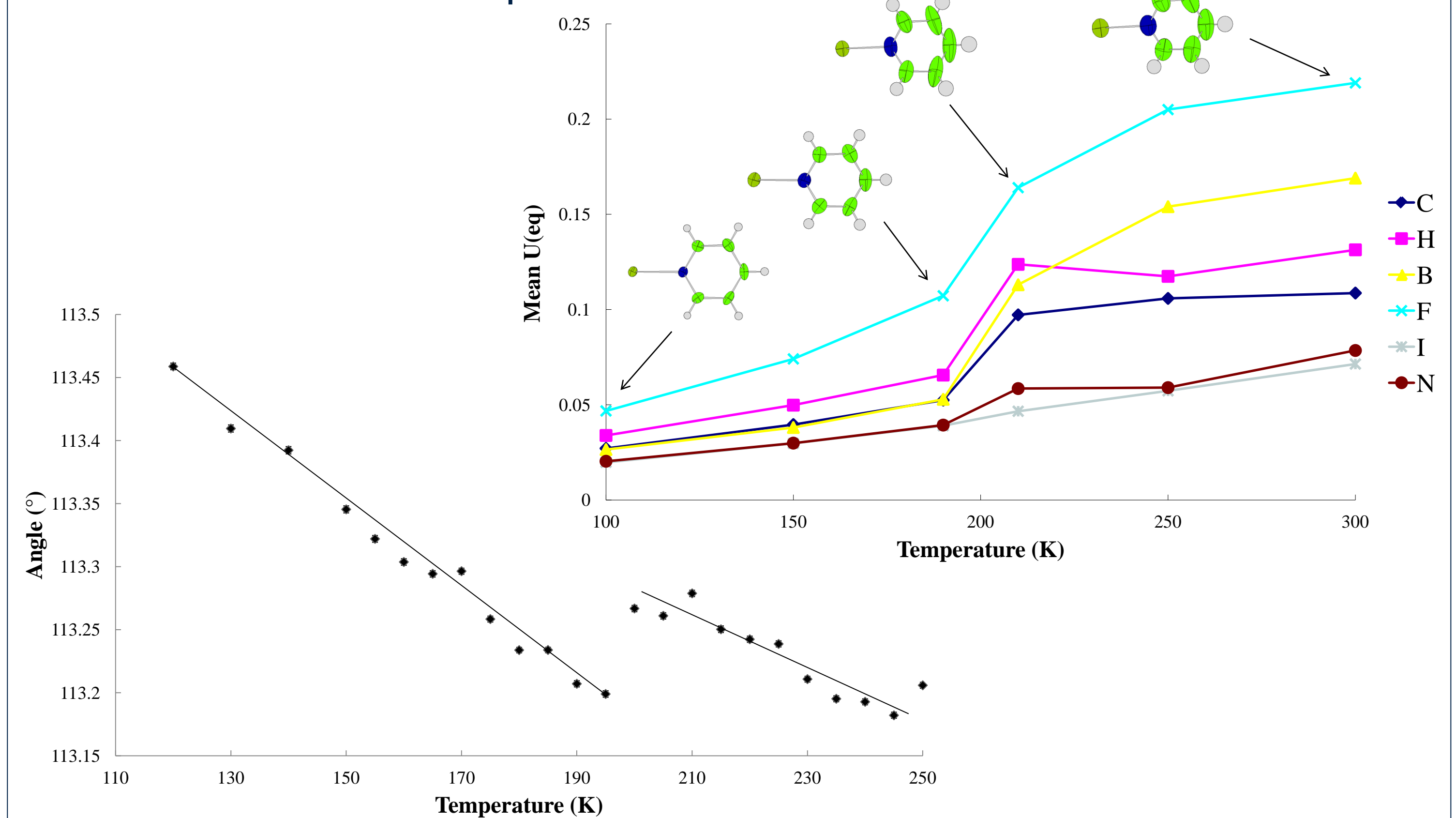


Figure 2 – The variation of β -angle with temperature (left) and the variation of equivalent isotropic displacement parameters with temperature (right). The effect of temperature on the ADPs of the pyridine rings are also shown.

Transient Phase

Reconstructed precession photographs were produced using the full data sets over a range of temperatures. These indicated that the phase transition was gradual. The appearance of additional reflections close to the transition temperature indicated the presence of a transient modulated phase.

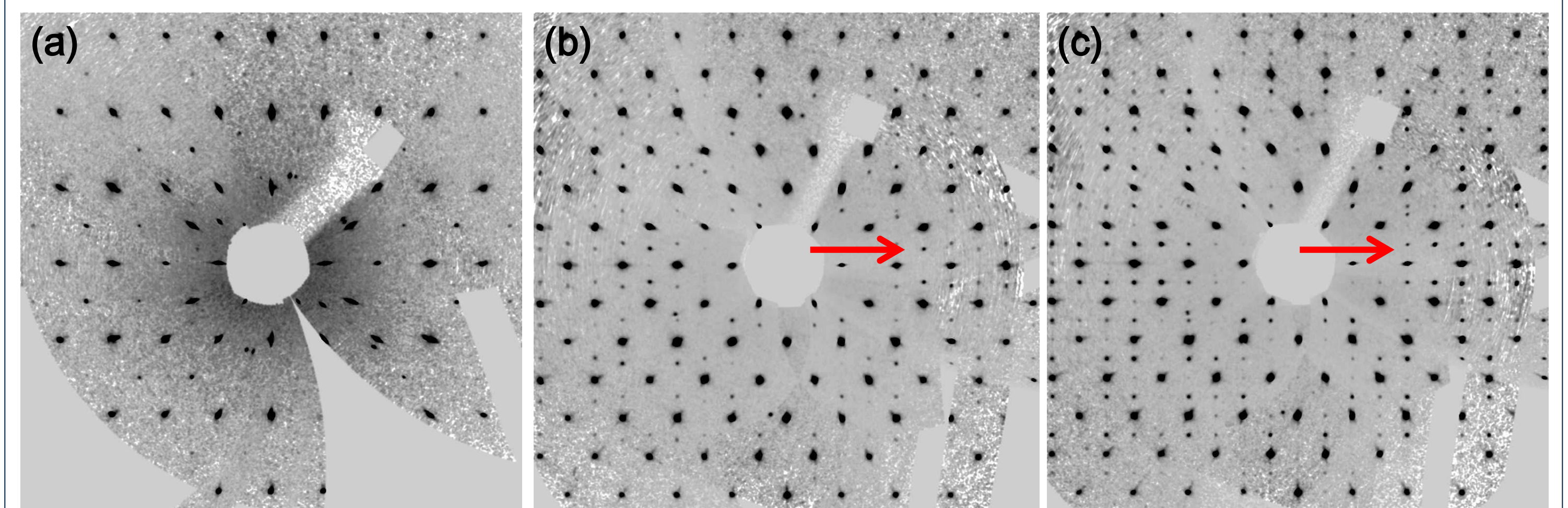


Figure 3 – Reconstructed precession photographs^[3] of the *hk0* layer of the cell at (a) 250 K (b) 210 K and (c) 150 K. The red arrows highlight the modulation shown with a 'zig-zag' pattern of reflections which straighten out.

The additional reflections are seen in (b) and (c) when compared to (a). It can also be seen that at 210 K the *hk0* where $k = 2n + 1$, the row is not straight, forming a 'zig-zag' pattern. This is thought to indicate modulation within the structure associated with the motion of the BF₄⁻.

Conclusions

The investigations undertaken have shown and characterised the phase transition of Barluenga's Reagent. This transition has been found to occur gradually with a transient modulated phase at the onset. The transition that occurs can be attributed to the BF₄⁻ counter ions present in the cell. The anion is found to be disordered at high temperature and becomes more ordered on cooling. This order-disorder behaviour is thought to be the driving force for the symmetry change that is observed.

References

- [1] J. M. Chalker, A. L. Thompson & B. G. Davis, *Organic Syntheses*, 2010, 87, 288.
- [2] P. W. Betteridge, J. R. Carruthers, R. I. Cooper, K. Prout & D. J. Watkin, *Journal of Applied Crystallography*, 2003, 36, 1487.
- [3] *CrysAlisPro*, Oxford Diffraction (Agilent Technologies), 2010.