Improving Our Understanding of Modulation in Molecular Materials

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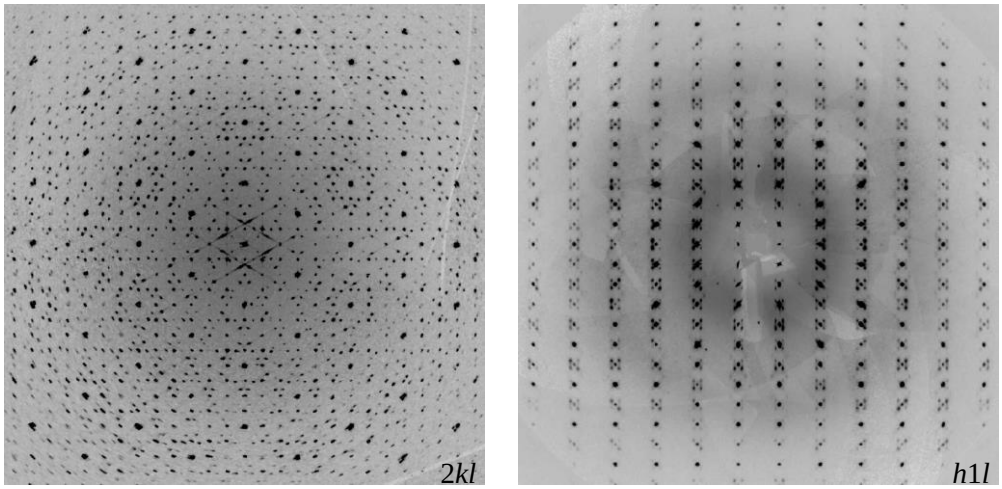
Single-crystal diffraction is the foremost technique used to give an understanding to how atoms and molecules pack in the crystalline solid state. As a maturing technique, data collections have been getting faster and faster, and structure determination is becoming more routine, with an increasing number of non-expert users collecting data, solving and refining structures before publishing their own results. However, with the advent of higher intensity laboratory X-ray sources, easier access to synchrotron radiation and more sensitive detectors, more and more molecular structures are showing alien features beyond the realms of conventional crystallography [1-3].

Within Chemical Crystallography at the University of Oxford, we see a huge variety of molecular materials and a wide range of crystallographic problems. Some structures are 'easy', some contain a lot of disorder, and others are too difficult for the users to handle for themselves. The Service studies crystalline materials from within Chemistry using single crystal diffraction. Herein we present some of the more challenging structures and our perspective on them.

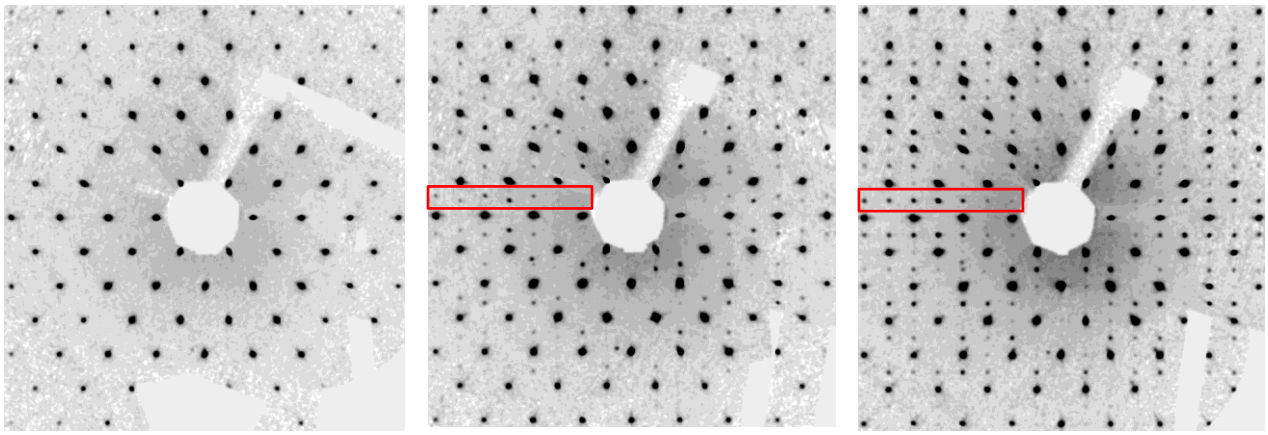
Though the concept of modulated structures is now fairly well established in solid state chemistry, the abundance of reported modulated molecular materials is less than might be expected. Often, the synthetic chemist is only interested in connectivity and proof of what they have made; they are not curious about additional peaks seen in a diffraction pattern (Figure 1). Sometimes by tweaking the synthesis and/or changing crystallisation conditions, the curious extra features disappear.



(a) (b)

Figure 1. Reconstructed precession images to 1.5 Å. The image to the left (a) was supposed to be a macrocyclo, but turned out to be an unwanted product [4]. The image to the right (b) is a solid state reaction with $H_{2\,(g)}$ [5].

When a concerted effort is made to study the appearance of additional satellite reflection and relating it to changes within the structure, valuable extra information can be gained concerning molecular packing and the crystalline state. One such example is found in Barluenga's reagent, IPy_2BF_4 [6], which has been shown to exhibit a transient modulated phase on cooling (Figure 2). Systematic studies on derivatives of Barluenga's reagent have been carried out in which the pyridine is replaced with 2,4,6-trimethyl pyridine, iodine with bromine and the BF_4 anion is replaced with other small anions including ClO_4, PF_6 and CF_3SO_3. Through small changes to the chemistry we can begin to understand how the crystal structure and the diffraction pattern are related and why satellite peaks may appear with the aim of improving our understanding of the mechanism governing the appearance of modulation in molecular materials.



(a) (b) (c)

Figure 2. Reconstructed precession images of the *hk*0-layer of IPy_2BF_4 collected at different temperatures. The image to the left (a) is collected at 300 K, the image in the middle (b) at 210 K and the image to the right (c) at 100 K. The boxes highlight the difference in *q*-vector between the two lower temperatures.

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5. A. I. Mckay, F. M. Chadwick, K. E. Christensen, A. L. Thompson, A. S. Weller, unpublished research.

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