Understanding the Growth and Short-Range Order of 1,5-Dichloro-2,3-dinitrobenzene (DCDNB) Crystals Using Atomistic Simulation and Single Crystal X-ray Diffuse Scattering.

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1,5-Dichloro-2,3-dinitrobenzene (DCDNB) has been the subject of extensive study over many years [1]. Earlier attempts to parameterize a disorder model for the diffuse scattering from DCDNB were the subject of a doctoral thesis by Heerdegen [2]. In a separate, more recent computational study of the DCDNB crystal [3], a comparison of lattice energies vs. ordering was assessed from super-cell models. Results concerning SRO or growth kinetics from these investigations remained inconclusive.

Diffraction patterns of DCDNB show strong and highly structured diffuse scattering (see Fig.1). These data were collected on the PSD diffuse scattering diffractometer in Canberra [4]. The major cause of the diffuse scattering is that each molecular site contains a molecule in one or other of two basically different orientations. However a number of issues that exist in this system make the task of obtaining a definitive description of the disorder quite problematical.

1. Optical experiments indicate that different growth sectors of a crystal show different optical activity and this raises the possibility that the structure and disorder may be different in different growth sectors of the crystal.
2. There is also a question of whether the average structure should be considered to conform to space group $P2_12_12_1$ or $P4_3$.
3. Though the disorder is nominally binary with either of two distinct orientations of the molecule occurring in any crystal site, this does not take into account that it is possible that the NO_2 groups are not always inclined to the plane of the benzene ring in the same way.
4. The NO_2 substituent at 3 (see Fig. 1) lies approximately in the benzene plane while that at 2 is approximately normal to the plane. The large displacement ellipsoids in the ORTEP plot seem to indicate that there is considerable variation of these angles.

Monte Carlo (MC) simulation of a model crystal has been used to explore this system. A model crystal comprising 48×48×24 unit cells with 4 molecules per cell was used. This gave calculated diffraction patterns of a comparable quality to the observed patterns. The computer simulation package ZMC [5] has been used for some of this work. In this paper we describe the problems that are inherent in the study of this material and report on the recent progress that has been made.

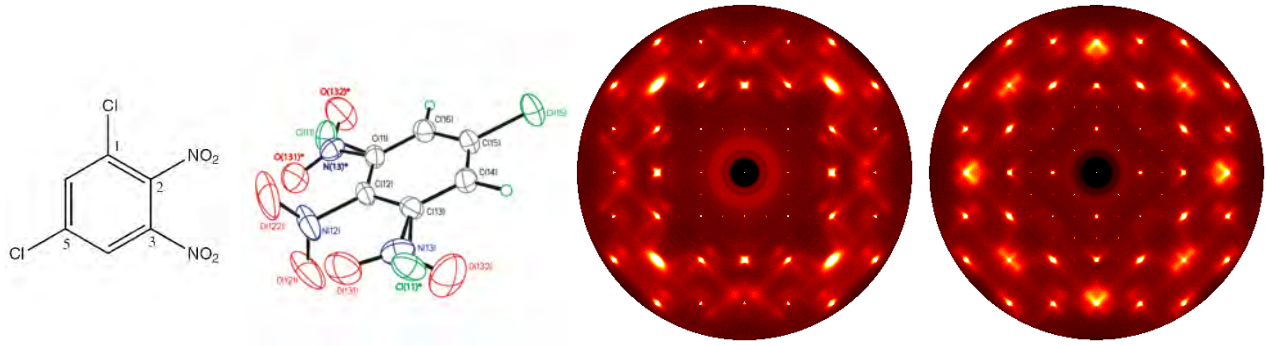

Figure 1. Chemical formula, ORTEP plot of the average molecular site and diffuse scattering in the *hk0* and *hk1* sections.

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