Modelling dynamic disorder in 3,3'-dimethoxybenzil, C_{16}H_{14}O_{4}

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Introduction

This work is part of an extended study of benzil (C_{14}H_{10}O_{2}) and derivatives which aims to understand the role that molecular flexibility plays in determining crystal packing and polymorphism [1, 2]. In this study diffuse X-ray scattering is used to probe both the inter- and intra-molecular correlated motions of a series of similar compounds in order to gain insight into how molecular motion influences crystal packing. In future studies it is hoped to apply the methodology to compounds of pharmaceutical interest which display polymorphism. In the present paper we present some preliminary results for the compound 3,3'-dimethoxybenzil, C_{16}H_{14}O_{4}, 33'-DMOB, (see Fig. 1). For this molecule the molecular flexibility is afforded by rotations about five C–C single bonds, defined by the dihedral angles $\phi_1 - \phi_5$.

Diffuse scattering arises from differences of the local structure of a crystal from the underlying average structure. Such differences (termed disorder) may be either static or dynamic in origin. For the compounds of current interest this disorder is purely thermal, and conventional crystal structure determination using Bragg scattering yields a perfectly normal average structure with no anomalous atomic displacement patterns. Nevertheless in all cases studied strong and highly structured thermal diffuse scattering is observed.

The analysis uses Monte Carlo (MC) simulation of a model crystal in which intermolecular interactions are modelled by harmonic springs and intramolecular forces by torsional springs. Diffraction pattern are calculated from the model crystal and these are compared to the observed data [1, 3]. Spring constants are adjusted iteratively until a satisfactory match between observed and calculated patterns is obtained. Then it may be assumed that the correlations in the model are similar to those in the real crystal, and since these arise out of the interactions in the model, these too may be considered representative of those in the real crystal.

Figure 1: Schematic picture of 33'DMOB, showing the internal degrees of freedom denoted by the angles $\phi_1 - \phi_5$. 

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Experimental

At 295K, 33′DMOB crystallizes in monoclinic spacegroup $C2/c$ with $a = 20.0790(4)$ Å, $b = 4.8086(1)$ Å, $c = 13.7747(3)$ Å and $\beta = 92.3620(9)^\circ$. The average structure had been previously reported [4], but the values used here were determined during the present study.

Diffuse scattering data were collected in the home laboratory using a diffuse scattering diffractometer (Cu K$\alpha$) [5] but subsequently more extensive data were collected on the 1-ID-C beamline of the XOR at the Advanced Photon Source (APS) using 80 keV X-rays and a MAR345 image plate detector. In the home laboratory $h0l$, $h1l$ and $h2l$ data were collected; Fig. 2 shows two of these planes in false colour. Key features to be noted are the structured regions of scattering in the $h0l$ layer (arrowed) and the fact that the strong peaks are more rounded when lying near a diagonal line running through the images (black arrows on Fig. 2b). For the synchrotron data a full 3D volume of reciprocal space was recorded but for analysis individual sections were extracted from this using the program Xcavate [6]. Fig. 3a shows the observed $h0l$ layer.

The Model Crystal

A Z-matrix description of the molecular geometry is used so that each molecule can be defined in the MC model using few variables — three Cartesian coordinates for the origin, three angles for the orientation and the internal degrees of freedom, in this case five torsion angles (Fig. 1). The intermolecular energy due to displacements is given by $E_{\text{inter}} = \sum_{cv} F_i (d_i - d_{0i})^2$, where $d_i$ is the length of vector $i$ connecting atoms on adjacent molecules, $d_{0i}$ is its equilibrium length and $F_i$ is its force constant. The sum is over all contact vectors (cv). Intramolecular energy for the model is given by summing the torsional energies of all molecules (mol). That is, $E_{\text{intra}} = \sum_{\text{mol}} \sum_i G_i (\Delta \phi_i)^2$, where $G_i$ is a torsional force constant and $\Delta \phi_i$ is its deviation from...
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Figure 3: $h0l$ plane of diffuse scattering from 33'DMOB: (a) Observed data collected at the APS. $(\sin \theta/\lambda)_{\text{max}} \sim 0.75\text{Å}^{-1}$. (b) Calculated from model determined using laboratory data.

Figure 4: Two layers corresponding to those in figure 2 calculated from the MC simulation. Non-data areas from the observed patterns have been applied to these calculations.

the equilibrium (see Fig. 1). By symmetry $G_2 = G_3$ and $G_4 = G_5$. $E_{\text{total}} = E_{\text{inter}} + E_{\text{intra}}$. $E_{\text{total}}$ is calculated for different, randomly-selected molecular configurations which are kept or rejected depending on their effect on $E_{\text{total}}$ ([1, 3]). After the model crystal reaches equilibrium, diffraction patterns are calculated using the program DIFFUSE [7].

Results

Initially the model was developed to fit to the laboratory data. Calculated $h0l$ and $h1l$ planes are shown in Fig. 4. The cross-shaped regions in the $h0l$ layer are well modelled and the diffuse spots grow increasingly elongated and less rounded further away from the line noted in Fig. 2b. After automated refinement of the model [1, 3], it was found that the strongest interactions lie predominantly in the $xz$ plane and propagate both in $x$ and $z$, and mainly connect with the methoxy groups. Other strong interactions lie in the $y$ direction. Methoxy to
methoxy interactions connecting molecules in \( x \) but not in \( z \) were weakest, while those running along \( z \) but not \( x \) were intermediate. Thus the molecules lie in sheets which extend along \( y \) and diagonally through the unit cells (see Fig. 5). Molecular flexibility was necessary for a good fit.

This model has more recently been used as a starting point in an analysis of the more extensive synchrotron data (see Fig. 3b). The \( h0l \) plane is well modelled even far out in reciprocal space, showing the predictive power of the model. The reciprocal space range of these data will allow more quantitative analysis of the torsional force constants through their influence on the relative intensities of diffuse peaks. Taking cuts normal to the \( h0l \) layer will give better information about correlations out of the \( h0l \) plane.

**Conclusions**

Significant steps have been made in modelling the structured thermal diffuse scattering from 3,3′DMOB. It appears that the structure can be considered as a stack of layers of molecules. Interactions are strongest within the layers. The layers interact weakly along the \( x \) direction but more strongly along \( z \), so shearing of the planes relative to each other is energetically likely. The molecule must be treated as flexible for a good model to be found.

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