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New Route to Local Order Models for Disordered Crystalline Materials: Diffuse Scattering and Computational Modeling of Phloroglucinol Dihydrate

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New route to local order models for disordered crystalline materials: Diffuse scattering and computational modeling of phloroglucinol dihydrate

Lynne H. Thomas,[1]* Gavin A. Craig,[2] Carole A. Morrison,[3] Anthony M. Reilly[3,4] and Chick C. Wilson[1]

[1]Department of Chemistry, University of Bath, Bath BA2 7AY, UK.

[2]Departament de Química Inorgánica, Universitat de Barcelona, Diagonal 647, 08028, Barcelona, Spain.

[3]EaStCHEM, School of Chemistry, Joseph Black Building, University of Edinburgh, West Mains Road, Edinburgh, EH9 3JJ, UK.

[4]Chair for Process Systems Engineering, Technische Universität München, D-85350 Freising, Germany.

[*]Corresponding author; e-mail: l.h.thomas@bath.ac.uk

Supporting information:
CIF for the experimentally determined structure; CIFs for the calculated MD local order models, including calculated thermal parameters; and coordinates for the input structures for the five different models investigated. This material is available free of charge via the Internet at http://pubs.acs.org

Graphical abstract:
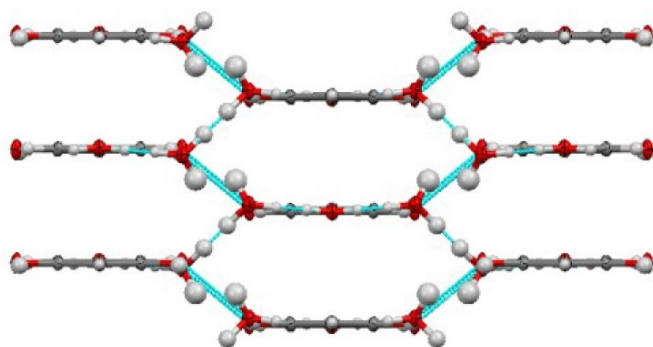
Synopsis:
An easily accessible method for generating short-range order models for disordered materials exhibiting diffuse scattering is presented and illustrated for the layered molecular material phloroglucinol dihydrate.

Abstract

A new, readily tractable route to determining short-range order models for materials exhibiting occupational disorder and diffuse scattering using first-principles solid-state quantum mechanical calculations is presented and illustrated with application to the disordered, layered molecular material phloroglucinol dihydrate.

Introduction

Traditional crystallographic structure determination involves finding the atomic positions and thermal parameters of all atoms in a crystal structure. However, it is often the imperfections in crystal structures which give rise to interesting physical properties such as the dielectric effect[1] and ferroelectric behavior.[2] Materials with such properties often exhibit disorder which shows some degree of short-range ordering. In these cases one might frequently observe structured diffuse scattering, the interpretation of which is not straightforward. The presence of structured diffuse scattering can be an indicator for short-range order which can be correlated over regions of only a few unit cells in some cases; a system in which there is only random disorder will not give rise to structured diffuse scattering. Currently, it is not possible to characterize the local ordering in such systems through conventional methods directly from diffraction data; this requires the generation and testing of many potential models through techniques such as Monte Carlo[3] or Reverse Monte Carlo modeling.[4] These methods require significant expertise and are often not transferable between systems. A route to models through more accessible means is therefore desirable to allow more routine analysis of the local ordering and, therefore, understanding of the driving forces behind resulting physical properties in this important class of materials.

The time-averaged structure obtained through diffraction methods is, however, a natural and valuable starting point for this modeling process, providing guidance and constraints on model generation through consideration of any unusual bond lengths and angles or by indicating any unusual shapes and sizes of the refined anisotropic thermal parameters. In this work we report on the use of condensed-matter first principles calculations as an *a priori* method of screening these possible models and as an *a posteriori* model validation technique, in terms of both their optimized structures and their stabilization energies. Favorable models can then be pursued with molecular dynamics (MD) calculations to study the time-evolution behavior of the proposed structures.

One crystal structure that has commanded our recent attention is the dihydrate of phloroglucinol.[5] At the very local level, the phloroglucinol molecule can adopt two different stable geometries (C_{3h} and C_s; see Figure 1). *Ab initio* calculations suggest that the energy difference between the minima resulting from optimizing these two candidate structures is very small (*ca.* 3 kJ mol^{-1}), with the higher symmetry structure favored as the global minimum.[6] The crystal structure of pure phloroglucinol also reports the molecular configuration as C_{3h},

with the OH groups located slightly out of the plane of the benzene ring to optimize the hydrogen bonding present.[7]
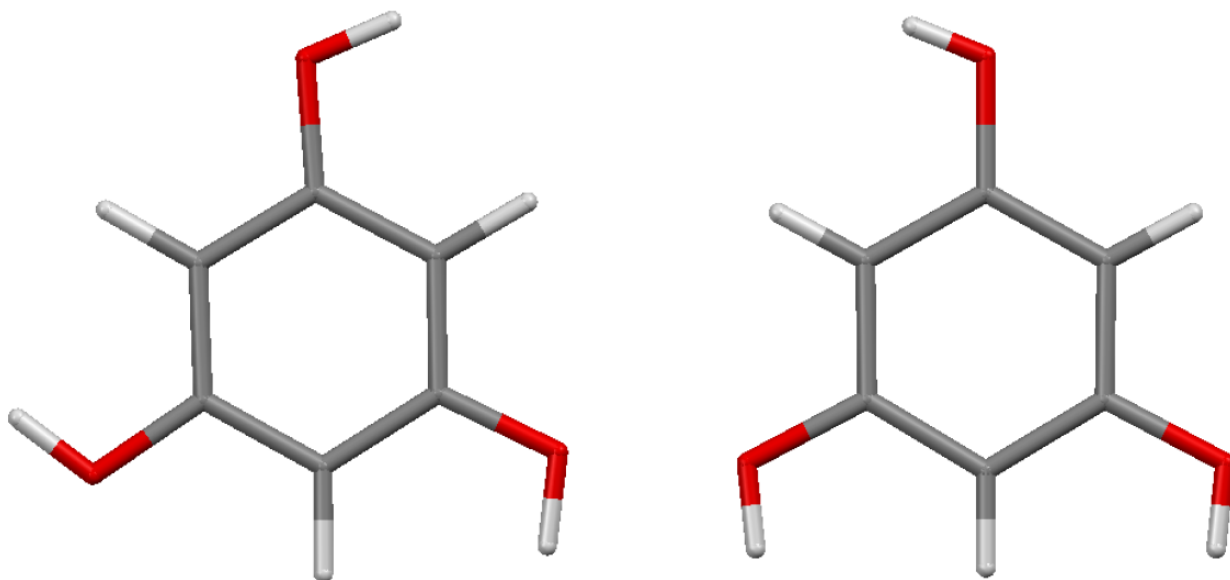

Figure 1. Two possible configurations for the local phloroglucinol molecule configuration, (left) C_{3h}; (right) C_s.

Introducing two molecules of water into the crystallographic asymmetric unit dramatically alters the crystal packing arrangement.[5] Pure phloroglucinol consists of interconnecting, almost perpendicular hydrogen bonded planes,[7] whereas the dihydrate is a layered material (Figure2). In the dihydrate, phloroglucinol molecules are connected to each other only through water molecules, some of which mediate hydrogen bonded chains of phloroglucinol molecules along the c-axis while others form hydrogen bonds between these chains, thereby constructing corrugated layers (Figure 2). These layers are stacked along the a-axis. The distinct, layered, extended packing arrangement of the dihydrate has a dramatic influence on its propensity to exhibit disorder and the nature of that disorder.

The crystal symmetry dictates that, in the average (X-ray) structure,[8] a mirror plane lies down the center of the phlorglucinol molecule perpendicular to the ring, and this in turn dictates that there is an inherent disorder in one of the OH groups, with the hydrogen atom precisely 50:50 disordered over two positions (Figure 2). This then has the consequence that order on a local length scale must be propagated down the hydrogen bonded chains, leading to long-range average disorder in this direction. This leads to strong streaks of diffuse scattering in the diffraction pattern along the c^{*}-axis. The hydrogen bonding around the oxygen atom must be symmetrical, as it lies on the mirror plane. On a local level, however, the hydrogen atom must exist in one of

the two positions, and this choice has a "domino" effect on the hydrogen bond pathways throughout the extended structure (Figure 3). Thus, one of the hydrogen atoms in the water molecule is also 50:50 disordered over two positions (H6 and H7). This can be deduced by considering the hydrogen bonds surrounding the water molecule (blue in Figure 3); atom H6 must be 50% occupied, as it is in the same hydrogen bond as the disordered hydroxyl group of the phloroglucinol molecule; likewise, a second water molecule, related by an inversion center (yellow in Figure 3) results in a 50:50 disorder between atom H7 and its inverted equivalent H7″. This requires the final hydrogen atom, H5, to be 100% occupied. The isotropic thermal parameter for this atom is larger than that of any other hydrogen atoms in the structure; this is likely to be due to the relatively weak nature of the hydrogen bond in which it is participating (O···O distance of 2.840(1) Å, cf. 2.7418(8) Å and 2.765(1) Å for the other two water hydrogen bonds). The breaking of the symmetry of the hydrogen bonds that results from this crucially forces the heavy atom positions to shift from their average positions, an important contributor to the generation of the observed diffuse scattering.
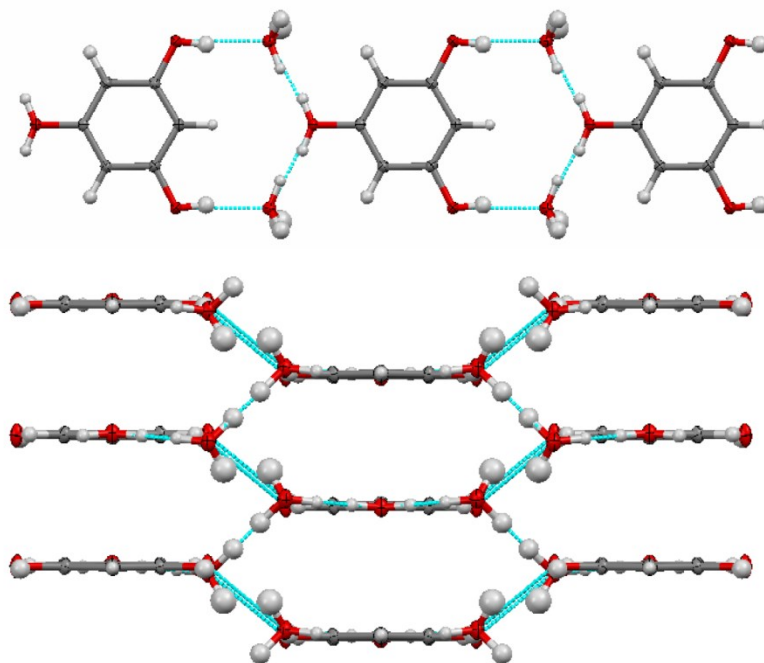
Figure 2. Top, the hydrogen bonded chains of phloroglucinol dihydrate; bottom, the corrugated layers of chains.

The presence of very strong diffuse scattering observed from the dihydrate material[5] strongly suggests that the local structure must involve cooperative hydrogen bonding over longer distances than those of the unit cell. Indeed, strong diffuse scattering is also observed at 100 K, with a sharpening of the diffuse features at lower temperatures suggesting a static model for the disorder is most likely. This local order is inherently linked to the behavior of the hydrogen atoms both on the phloroglucinol molecule and on the water molecules.

Therefore, obtaining definitive hydrogen atom positions is vital to understanding the driving forces behind the short-range order in this material. Herein lies the problem: hydrogen atom determination from X-ray diffraction data cannot be regarded as reliable, and in any case, the "domino" effect induced by the disorder of the hydrogen bonded network makes the identification of starting models for local ordering difficult. The average model clearly gives an inadequate description of the intermolecular interactions on a local length scale. As indicated above, however, the average structure can be used as a valuable constraint on any local order models obtained. Individually the models must show a good correlation to the average structure, since most of the atoms are well ordered and well defined. These are powerful constraints.
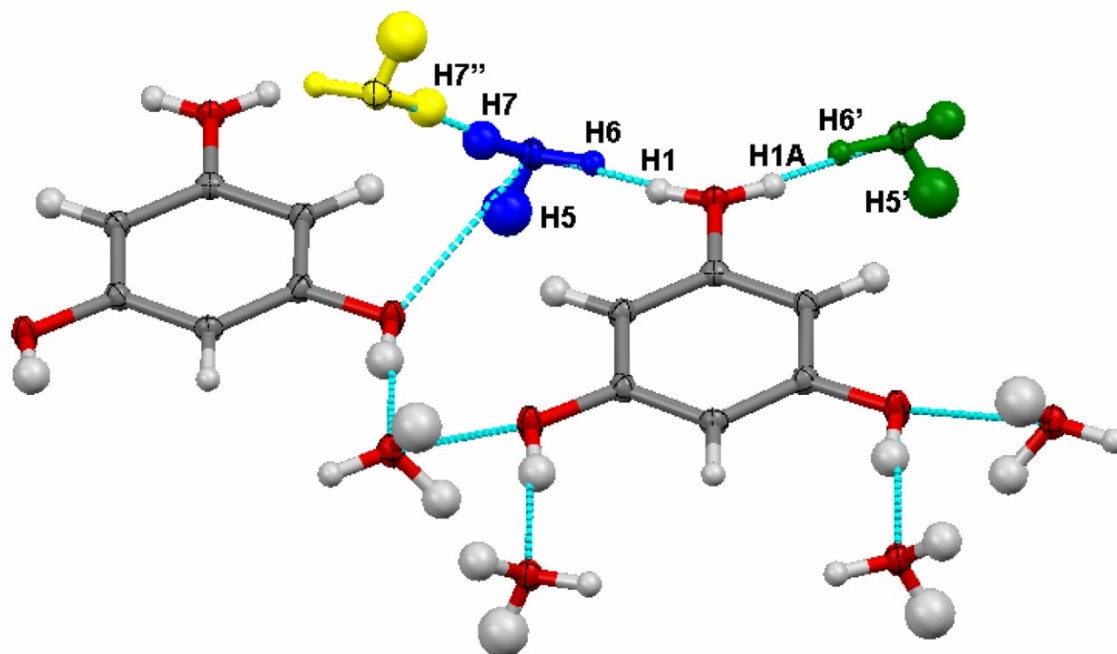
Figure 3. Domino effect on the hydrogen bonded network induced by the disorder of the hydroxyl group on the phloroglucinol molecule (labeled H1 and H1A) and the consequential disorder of the water molecule (H5 is fully occupied, H6 and H7 are 50:50 disordered). The symmetry equivalent water molecules participating in the domino effect are colored; the effect can be explained with reference to the two possible configurations of H1 (H1 and H1A). If the H atom occupies site H1, then the blue water molecule will adopt the orientation H5–O–H7, and the yellow water molecule will be oriented so as not to occupy H7″. The green water will be oriented as H6′–O–H5′. In the case where H1A is occupied, the blue molecule will adopt the H5–O–H6 configuration, and H6′ on the green molecule cannot be occupied.

Figure 4. Comparison between the unit cell contents in the average X-ray determined structure and, in green, the computationally determined models: left, $P2_12_12_1$; right, $Pn2_1a$. Clear agreement between the optimized hydrogen atoms in the calculations and those tentatively assigned from the X-ray diffraction can be seen. The nonoccupied H atom positions from the experimental data have been excluded for clarity.
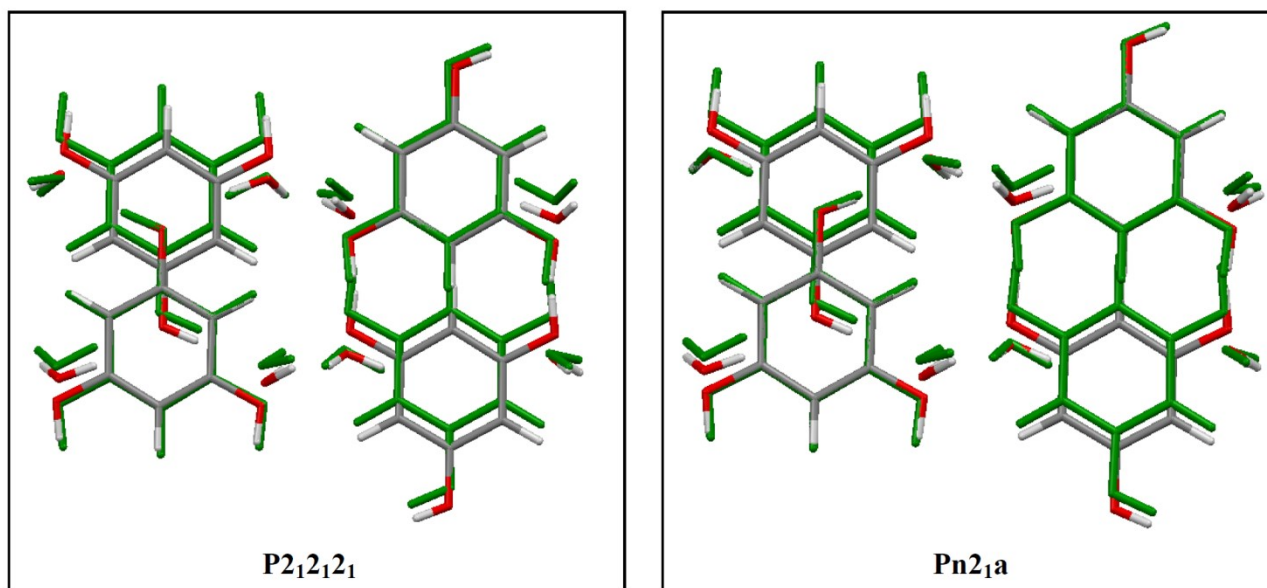
In an effort to overcome the problem of developing and assessing plausible disorder models for this system, we turned to computational modeling.[9] In total five different starting models were constructed, all of which were based on the experimentally determined average structure and ensured that the number of hydrogen bonds was saturated: two models were based on the local structure conforming to symmetry C_{3h} (space group $P1$) and three to C_s (two with space group $Pn2_1a$ and one with $P2_12_12_1$) (see Supporting Information for more information). The atomic positions in all five trial crystal structures were then optimized (note, unit cell vectors were fixed at experimental values). This quick and straightforward process provided immediate results. The C_{3h} local symmetry option was not particularly stable, with some molecules in the crystal lattices in both $P1$ models undergoing conversion to the C_s form. Moreover, the average energy of the asymmetric unit (comprising one phloroglucinol and two water molecules) was around 30 kJ mol^{-1} higher in the $P1$ space group settings than for the $Pn2_1a$ and $P2_12_12_1$ forms; this effectively eliminates the $P1$ model from further consideration.

The three lowest energy computed structures differed in energy by less than 6 kJ mol^{-1}. However, only two of these closely matched the heavy atom positions from the X-ray diffraction data (Figure 4), and their energy difference was much smaller (ca. 1 kJ mol^{-1}). The third model (with $Pn2_1a$ symmetry) showed significant displacement of the water molecules away from the disordered phloroglucinol hydroxyl group and, in addition, predicted the ordered hydroxyl groups on the phloroglucinol molecule to twist out of the plane of the

molecule. These represent significant differences from the experimental average structure and would be expected to be clearly visible in the thermal parameters of the non-hydrogen atoms. For these reasons, this model was discounted. In the remaining two models, the hydrogen atom positions optimize to positions close to those tentatively suggested by the X-ray diffraction data and support the disordered assignments of these atoms, in particular for the relatively unreliably determined hydrogen atom positions on the water molecule. The heavy atom positions for the water molecules are found to shift, as expected, depending on the position of the hydrogen atom on the disordered hydroxyl group (Figure 5). The O–H···O distances from the phloroglucinol to the water molecules, which in the average disordered structure are equal with value 2.7418(8) Å, are found to vary depending on whether the hydrogen in the ordered model is located on the phloroglucinol (∼2.718 Å) or the water (∼2.756 Å), in both computational models. This significant effect on the heavy atom positions resulting from the hydrogen order/disorder models is important, since a model for disorder which only resulted from variation in the hydrogen positions would not give rise to such strong diffuse X-ray scattering due to the inherently weak scattering observed from hydrogen atoms. However, the systematic shifts in the heavy atom positions, suggested by the computational modeling and arising as a direct consequence of the local ordering of the hydrogen atom positions, could be anticipated to provide a contribution to the diffuse scattering.
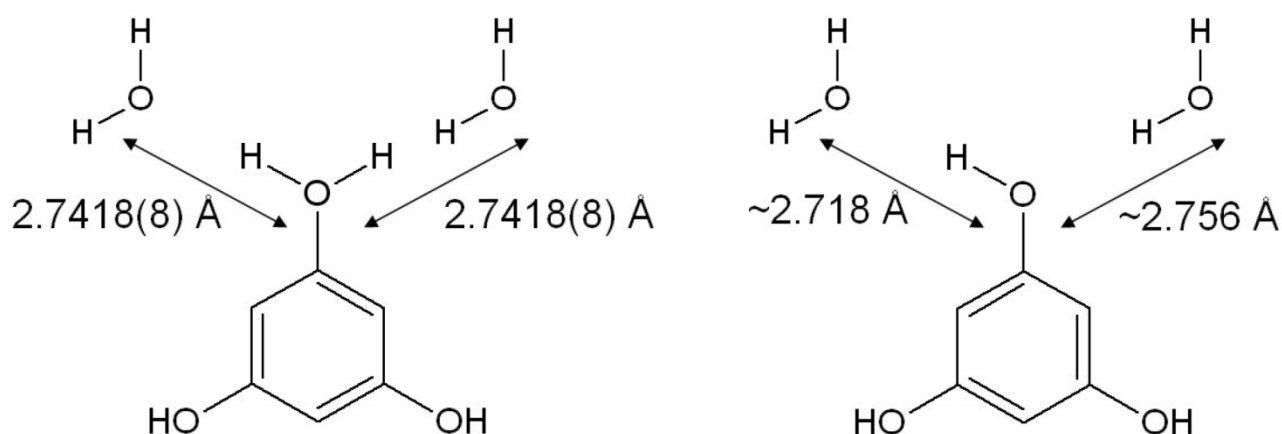
Figure 5. Heavy atom shifts resulting from the breaking of the symmetry when moving from the disordered average structure to the (computationally determined) candidate ordered structures. The hydrogen bond distances from the phloroglucinol to the water molecules are found to vary depending on whether the hydrogen is located on the water or on the phloroglucinol molecule. Thus, the hydrogen atom disorder can be seen to induce displacements of the heavier atoms.

The two computed structures belong to polar space groups, and thus, their inverted structures are also possible. Note the observed, experimental crystal structure cannot be explained solely on the basis of one or other of the models proposed here. Rather, the structural description found from standard refinements based on the (Bragg) X-ray data will result from a weighted average of these structural models through a supercell, which will contain localized regions of both lower symmetry models and be guided by the critical test of agreement with the experimentally determined average structure. A combination of all four potential (polar) models generated here therefore provides a route to the average X-ray determined structure. The exact proportions of each cannot be determined by the current analysis, but the experimental X-ray structure provides a significant constraint when rationalizing the plausibility of the models obtained. Thus, it is consistent to describe the macroscopic crystal in this system as an intimate, lattice-level combination of four ordered crystalline forms coexisting within the same crystalline matrix. The space groups found are also consistent with the structure adopted by pure phloroglucinol, as this material also crystallizes in an ordered noncentrosymmetric space group (in this case $P2_12_12_1$).

In addition to the geometry optimization process, it is useful to pursue the resulting optimized structures with MD simulations, in order to check that the time-averaged computed structures are consistent with the time-averaged experimental structures. Provided that the dynamics are run for long enough (typically of the order of at least 20 ps), then computed anisotropic thermal displacement parameters can also be obtained, which offers further direct comparison with the experimental study.[10, 11] This is done by using the positions adopted by the atoms during the molecular dynamics simulation to calculate numerically the variances and covariances of each atom, which correspond to the crystallographic thermal parameters. A visual comparison for both the $P2_12_12_1$ and $Pn2_1a$ symmetry settings is shown in Figure 6. The calculated and experimental thermal ellipsoids are drawn at the 50% probability level and are representative of the thermal movement of the atoms. It should be noted, however, that the MD simulations were run at a much higher temperature than the experiment. The reasons for this were 3-fold: first to encourage a faster equilibration time and second to minimize the effects of quantum tunneling and zero-point energy contributions that are absent in this type of simulation and that are known to have a strong impact on the thermal parameters of light atoms. Third, it should be noted that as the MD simulations were performed on a $1 \times 1 \times 1$ crystallographic unit cell, we can only sample the vibrational modes that are contained within that space. Any low energy lattice mode vibrations, which may need two or three (or more) unit cell representations will be absent from our simulation. Our previous work on simulating the thermal ellipsoids present in the crystal structures of ammonia and nitromethane demonstrated the importance of all of these points,[10, 11] but it does raise the issue of what temperature is best to choose in the MD simulation. The agreement obtained with the experimental data in the high temperature MD runs for both models is equally good, giving further evidence of the applicability of both calculated models in the experimental average structure. Both show some elongation of the oxygen atom thermal parameters, in particular out of the plane of the benzene ring; this is more marked in the calculated models than in the experimental data. The use of experimentally determined thermal parameters has

previously been shown to indicate and constrain short-range order models in a similar system,[1] and thus, the ability to replicate thermal ellipsoids from first-principles calculations is highly desirable.
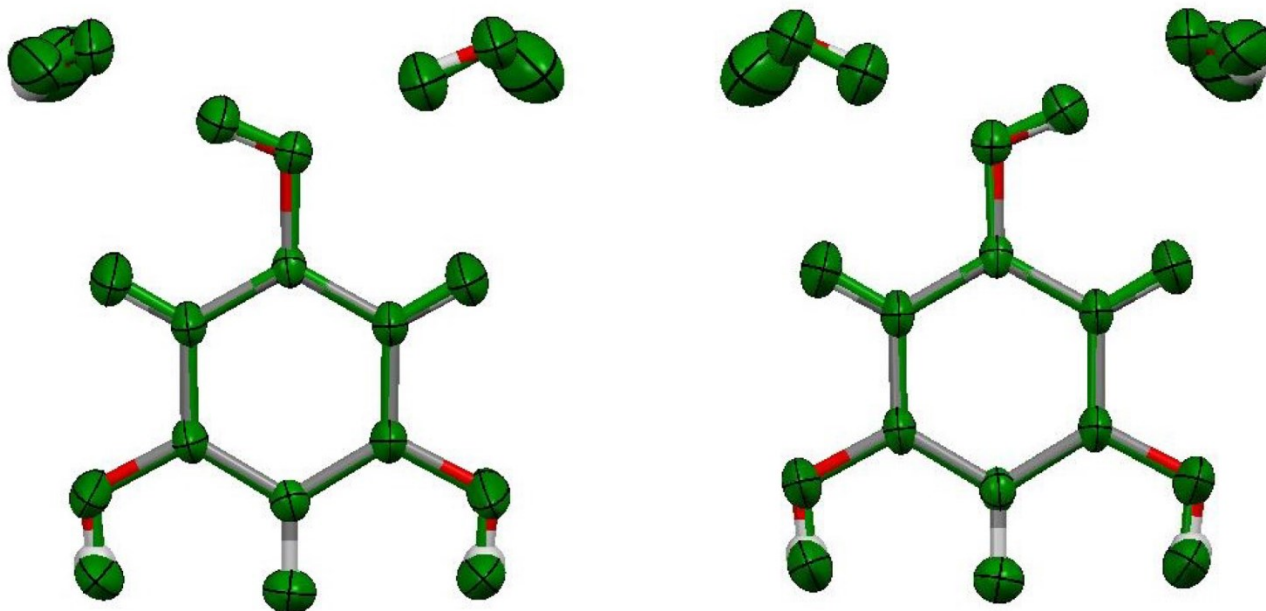

Figure 6. Overlay of the thermal ellipsoids of the experimental (100 K) and calculated (green, MD simulations at 500 K[10, 11]) structures for the $P2_12_12_1$ asymmetric unit (left) and the $Pn2_1a$ (right). The unoccupied H atom positions derived from the average experimental structure have been omitted for clarity.

In this communication, we have demonstrated a new methodology to solve the disordered crystal structures of materials exhibiting diffuse scattering by combining X-ray diffraction data with condensed matter first-principles calculations. In essence, this offers a route to generate consistent local order molecules in a highly disordered crystalline system, where the average structure does not adequately describe the short-range order. *Ab initio* calculations were used first in a screening capacity, reducing the number of local-order models with saturated hydrogen-bonding networks that need to be considered from five to two. Combining these models, along with their centrosymmetric inverted counterparts gives a structure which is consistent with the heavy-atom average structure derived from the X-ray data. In this way, the calculations have been used in a structure completion capacity, giving supporting evidence to tentative assignments of disordered hydrogen atom positions. The stability of these local-order models was then tested further by molecular dynamics simulations, which demonstrated that the atomic thermal motions in these simulated lattices were broadly consistent with the experimental parameters. Consistency between both the calculated energy-minimized static structures and the dynamical time-averaged models, and the experimentally determined structure has been achieved. This method thus shows considerable promise in streamlining the model generation process for

describing short-range order in highly disordered crystalline materials and is easily transferable to other systems. We intend to study this system further, using these initial starting models to generate short-range order in this system through Monte Carlo modeling to qualitatively match the observed diffuse scattering. However, the method presented here, in its own right, has the capability to qualitatively explain local ordering patterns in phloroglucinol dihydrate and other similarly disordered systems.

Notes and references

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13.5455(9), $c = 8.0423(3)$ Å, T = 100(2) K, $Z = 4$, μ = 0.132, $R1 = 0.0357$ for 818 data with $Fo > 2$ $\sigma(I)$, $wR2 = 0.1086$ for 860 unique data (all data 4781). Crystallographic data have been deposited with the CCDC (CCDC-797470).

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