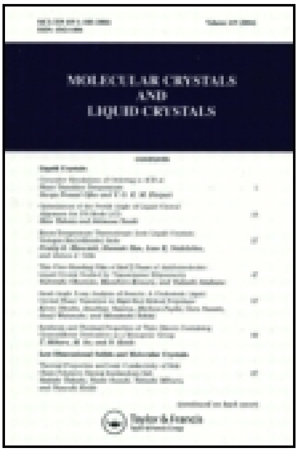

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Gerard P. Hastie [a], Joy Johnstone [a], Kevin J. Roberts [a] [b] & Elaine M. Walker [a]

[a] Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, UK

[b] CLRC Daresbury Laboratory, Warrington, UK

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THE EFFECT OF SURFACE MOLECULAR CONFORMATIONAL CHANGE ON MORPHOLOGY: A STUDY OF BENZIL (0001)

GERARD P. HASTIE, JOY JOHNSTONE, KEVIN J. ROBERTS[+] and ELAINE M. WALKER,
Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, UK
[+]also at CLRC Daresbury Laboratory, Warrington, UK

Abstract Computational methods increasingly aid in the understanding of the processes which take place during crystal growth, especially in their use for crystal morphology predictions. Such calculations, based on solid-state structure, rely on three assumptions which generally work well for molecular solids. One of these assumptions is that the crystal surface is a perfect termination of the bulk, i.e. surface/bulk equivalence. In this work, XAS data, which indicates a difference between the surface and the bulk structure of the benzil (0001) surface, has been rationalised through molecular surface minimisation techniques.

INTRODUCTION

The process of crystallisation is an important and energy efficient method for the separation and purification of bulk and fine chemicals. Other similar techniques, such as distillation, are often precluded where the processing of particulate materials are concerned and when product stability and environmental factors are important. Due to an increasing focus on the manufacture of speciality products within the chemical industry and the increased requirements for process control and product differentiation, it is clear that the expectations of the crystallisation process are likely to become greater[1]. As a result of this increased expectation, there is in turn a need for an improved understanding of the underlying molecular processes taking place during the crystallisation event.

This paper reviews some of the methods used for the prediction of crystal shape and illustrates the theoretical limitations. Such restrictions are then rationalised with the aid of ultra-soft polarised X-ray absorption spectroscopy data together with molecular minimisation calculations. The system of interest is the hexagonal phase of the aromatic molecular species, benzil ($((C_6H_5C{=}O)_2)$) which crystallises in a trimolecular trigonal space group, $P3_12_1$ with cell dimensions $a = 8.409Å$, $c = 13.672Å$ and $\gamma = 120.0^\circ$ (see figure

1)[2]. In this molecule we have two phenyl rings joined together with two *trans* carbonyl groups, with the latter providing a degree of flexibility.

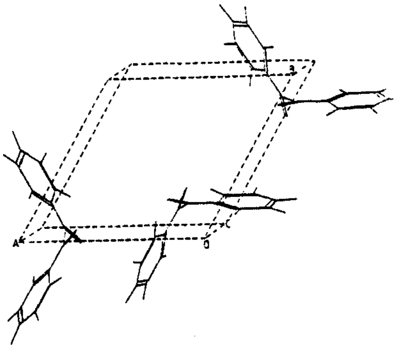

FIGURE 1 Crystallographic unit cell of benzil

Prediction of Morphology and Assumptions

Likely growth forms are selected using Bravais-Friedel-Donnay-Harker laws[3-5] which define the importance of a crystallographic form (hkl) as being directly dependent upon it's interplanar spacing d_{hkl} (after allowances have been made for space group symmetry). These growth planes can be predicted with available computer programs[6,7] and surface attachment energies (E_{att}) can then be calculated using the approach of Hartman and Perdok[8]. E_{att} is defined as the energy released on the addition of a growth slice to the surface of a growing crystal, which is related to the crystallising energy E_{cr} by the following equation:

$$E_{cr} = E_{slice} + E_{att} \qquad (1)$$

where E_{slice} is the energy released upon the formation of a slice of thickness d_{hkl}. E_{slice} and E_{att} are calculated using a pairwise summation of the potential energy involved in the intermolecular interactions between a central molecule and all the molecules within and outwith, respectively, a slice of thickness d_{hkl}. The position of the growth slice within the crystal structure can be adjusted with respect to a limiting sphere in order to obtain the most stable slice, i.e. that with the most negative energy. When more than one molecule is present in the unit cell, an average energy value is obtained over all molecular positions. For low supersaturations, the growth rate of a given crystal face can be taken as being proportional to E_{att}[9-11] and hence faces with the lowest attachment energies will be the slowest growing and have the greatest morphological importance. The predicted crystal shape, based on such calculations can be drawn by making a Wulff plot[12] using the gnomonic projection for which there are available computer programs[13,7]. The accuracy of the calculation can be estimated through a comparison of the E_{cr} value achieved and the experimental sublimation enthalpy of the material. These are related through equation 2, where the 2RT term is a correction factor which represents the difference between the gas phase enthalpy and the vibrational contribution to the crystal lattice enthalpy[14].

$$E_{cr} = \Delta H_{sub} - 2RT \qquad (2)$$

The utilisation of this approach in the case of crystal growth from liquid phases demands the use of three *ad hoc* assumptions, see for example reference 15:

- *equivalent wetting*: it is assumed that solid-fluid intermolecular bonds formed at the interface are the same as they would be if formed in the bulk solution;
- *surface/bulk structure equivalence*: it is assumed that the surface structure reflects a perfect termination of the bulk structure, i.e. no surface relaxation takes place;
- *the proportionality relationship*: it is assumed that the three bonds associated with the crystallisation process (solid-solid, solid-fluid and fluid-fluid) are in the same ratio for any crystal surface (hkl).

Despite this, many studies have revealed a surprisingly reliable correlation between observed and predicted morphologies, particularly in the case of molecular crystals[15,16] This probably reflects the fact that the nature of the interactions between the molecules, in mother and solid phases (following growth) consist of relatively weak isotropic van der Waals forces[10]. However, recent studies[17,18] have shown that where there is a degree of flexibility in the molecular system, surface relaxation can be expected to have an effect on the resultant predicted crystal habit.

Prediction of the Morphology of Benzil

The Dreiding potential set[19] along with charges generated via MOPAC VI[20] and the MNDO Hamiltonian was found to give an accurate representation of the benzil lattice energy, using the computer program HABIT95[21] with the use of a 30Å summation limit. The calculated lattice energy was -25.93 kcal/mol compared with an experimental value of -24.70 kcal/mol, which was determined from sublimation enthalpy data[22].

The ten most important morphological forms were identified using BFDH Laws[3-5] and their respective attachment energies were determined.

The resultant morphology shows a good agreement with experimental data from the undercooled melt[23]. Figure 2 shows the morphology produced. In the predicted model, a habit, elongated along the crystallographic c-axis, is produced with dominant {10-10}, {0-110}, {11-20} and {1-101} faces, capped with {0003}, {10-12}, {1-102} and {0-112} forms. The main difference between the experimental and predicted morphologies is the size of the {0003} face. The growth rate of this form is underestimated in the prediction, as in reality this face grows out of the habit, leaving less truncated edges and a more elongated morphology.

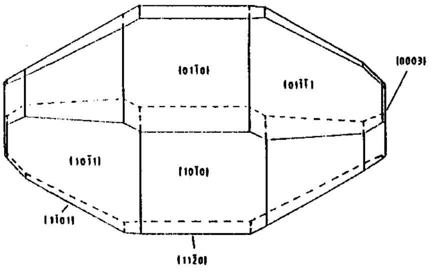

FIGURE 2 Predicted AE morphology of benzil

In order to understand this apparent discrepancy, the (0003) surface has been visualised with the aid of molecular modelling techniques (see figure 3). This reveals the phenyl rings within the benzil molecule to lie perpendicular to the surface, with the oncoming layer involved in π-π bonding between the phenyl rings. It has been suggested[17,18] that neglecting to consider the relaxation of surface molecules for specific habit faces can result in errors within morphological predictions. With this possibility in mind, we have used X-ray absorption spectroscopy (XAS) and molecular minimisation techniques to examine benzil (0003).

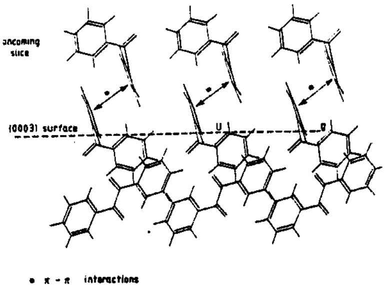

FIGURE 3 (0003) surface of benzil, with oncoming layer involved in π-π bonding

XAS SPECTROSCOPY

XAS, using synchrotron radiation provides the capability to probe the structure of interfacial systems[24,25] without recourse to the use of UHV based analytical tools such as electron microscopy and surface analysis (e.g. XPS/SIMS). As XAS does not demand long-range order or ultra-clean surface preparative methods it is a particularly optimal tool for the structural analysis of "real" chemical systems such those prepared by crystal growth from fluid.

X-ray absorption spectra taken of a condensed material exhibit an oscillatory structure which can extend up to 1000eV or more beyond the absorption edge (near-edge structure).

X-ray Absorption Near-Edge Structure (XANES) spectroscopy is the region of the absorption spectrum from the absorption edge threshold and extending above the edge by about 50eV. These intensities correspond to the situation where a K-shell electron has been excited to localised molecular orbitals. The properties of these orbitals are influenced by the bonding in the molecule and so XANES spectroscopy can distinguish certain structural features, e.g. it can identify transitions to a variety of empty states such as C-C, C=O and C=C σ^*, C=C and C=O π^*. The XANES spectrum yields mainly orientational information and has been extensively used for the structural investigation of chemisorbed molecules. However, to examine low atomic number elements e.g. C, N and O, requires ultra-soft (very short wavelength) X-rays. These are heavily attenuated in air and so require that the beamline be under vacuum. Only recently have advances in window materials and detectors made it possible to study such species under realistic thermodynamic conditions. The X-rays of the synchrotron are approximately linearly polarised and can be used to perform orientational studies as the incoming X-ray beam will produce a peak of maximum intensity when the electric field vector of the beam is parallel to a particular bond orbital. Therefore, by altering the angle at which the beam strikes a sample and noting the response, the orientation of that orbital, with respect to the substrate, can be determined. Electron yield detection probes to a depth of about 2nm, while fluorescence yield probes to about 200nm and so can be counted, for thin samples, as a bulk technique.

A (0001) slice (equivalent to (0003)) was cut from a benzil single crystal and attached to a steel sample holder using silver loaded epoxy resin. The XANES spectra were recorded over the region 280-320eV on beamline U1A at the National Synchrotron Light Source at Brookhaven National Laboratory using an extended range grasshopper (ERG) monochromator. The sample chamber provides for measurements to be made in fluorescence and electron yield modes. A conventional channeltron electron yield detector and a fluorescence detector were used. The sample chamber, which is separated from the UHV beamline by a differentially pumped aluminium window, is maintained at moderate pressures (ca. 1×10^{-6} mbar) and is thus suitable for examination of organic materials. XANES spectra were obtained at angles of incidence from glancing (10°) to normal (90°), with respect to the substrate, in increments of 10°.

Complete orientation scans for both surface (electron yield) and bulk (fluorescence yield) are shown in figure 4. Consider first the surface sensitive electron yield data, there is only one orientation dependent peak, B. It increases in intensity with decreasing angle of X-ray incidence. The peak shape is characteristic of a σ resonance and has energy corresponding to that expected for the C-C σ^{*26} transition. This means, then, that on the surface of the (0001) face, the benzil molecule is pointing out of the plane, at approximately right angles to the sample holder. Peak A is attributable to the C=C π* transition. It shows no orientation dependence, which suggests that the planes of the rings are roughly perpendicular to the sample holder, but a little twisted with respect to each other, such that a small intensity is observed. In the bulk, no orientation dependence is observed, reflecting the fact that the orientation effect of one ring is cancelled by the other. Peak A however, is much more intense than in the electron yield data, indicating that the aromatic rings are oriented such that the electric field vector of the X-ray beam is aligned with the π orbitals. Since this transition shows no orientation dependence, the rings must be oriented, one flat and the other "edge-on" (see figure 5).

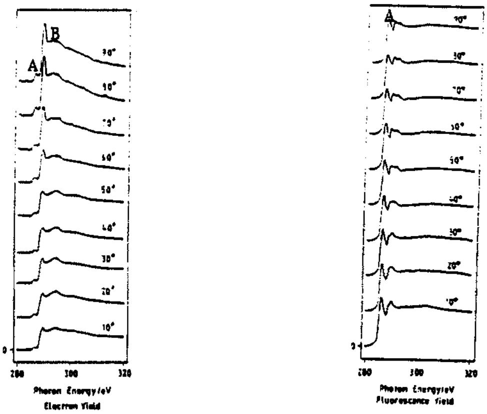

FIGURE 4 Orientation scans of benzil (0001).

Therefore, the data clearly show that the structures of the bulk and the surface are not the same. The bulk structure has the rings approximately at right angles to each other, while in the surface, the molecule is flatter, i.e. a relaxation of the structure occurs at the surface of the (0001) face.

MOLECULAR MINIMISATION STUDY OF BENZIL (0003)

During an energy minimisation, the atomic co-ordinates and unit cell (if present) are adjusted in order to optimise the molecular energy. The energy is calculated using a force field energy expression which is the basis of the molecular mechanics calculation. The entire structure can be moveable or selected atoms can be fixed. The minimisation is terminated when the root mean square force (RMS force) is below a specified convergence value (0.1 kcal/mol/Å). Setting up the energy expression involves specifying a number of variables, including the energy terms to be included and the methods and parameters used for calculating non-bond, hydrogen-bond and electrostatic interactions. The moveable and fixed atoms and those which are to be excluded from the energy calculations must also be defined.

During these calculations a co-ordinate minimisation using the conjugate gradient 200 algorithm[27] was used. This makes use of previous minimisation steps, as well as the current gradient to determine the next step, resulting in rapid convergence. The method converges to the minimum energy in the order of N steps, where N is the number of degrees of freedom. The Dreiding force field[19] was used in conjunction with this minimiser.

In order to rationalise the results of the XAS study, a slab of the (0003) surface was cleaved and the effect of minimising one movable benzil molecule on a fixed surface was investigated. This showed that while the bulk crystal restricted the movement of one phenyl ring, the other moved out of plane substantially, which could alter the subsequent π-π interactions during crystal growth. Two molecules, followed by three molecules were then minimised together, to show that the same effect occurred.

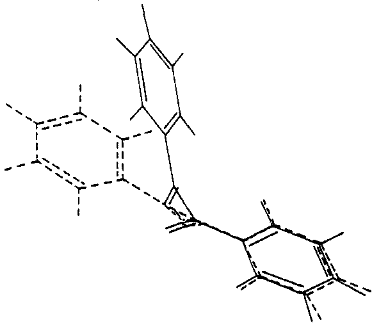

FIGURE 5 Benzil molecular structure before (solid) and after (dashed) minimisation

Figure 5 illustrates the difference in the benzil structure before and after minimisation, showing a 3° change in the carbonyl-carbonyl angle and a 58° degree change in the torsion of the phenyl ring, in relation to an oncoming crystal slice. This indicates that during crystal growth, the positioning of the oncoming benzil molecules does not need to be as precise as one might imagine, due to π-π interactions and so more growth units can be attracted to the surface and so the slice will grow much faster, resulting in its disappearance from the observed crystal habit, thus rationalising the apparent underestimation for E_{att} for the (0003) surface.

CONCLUSIONS

Here we have shown that while in the case of most molecular crystals, the assumptions used for predicting crystal shape are sound, in some cases, e.g. where there is some molecular flexibility, they break down. This results in a small degree of inconsistency between the predicted and experimental models. Here we have rationalised the discrepancy in the morphological prediction of benzil through the use of XAS and molecular minimisation methods. This shows that some form of surface relaxation does occur, resulting in an increased opportunity for crystal growth on the (0001) face.

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