Direct evidence for surface reconstruction on organic solid surfaces: benzil (0001)

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A molecular modelling study of the (0001) surface of benzil reveals evidence for surface reconstruction associated with a change in molecular conformation effected *via* a relaxation of π–π intermolecular interactions which are strong in the solid-state but absent on the exposed surface. This is confirmed by an examination of a single crystal sample using ultra-soft polarised X-ray absorption spectroscopy at the C K-edge.

Over the past 20 years UHV surface science techniques have made a dramatic and substantial contribution to our understanding of the surface crystallography of metals and semi-conductors and, to a lesser extent, simple AB components such as oxides. However, despite the importance of surface structure in understanding and controlling the processing of organic solids, particle formation, comminution, colloidal dispersion, tabletting *etc*., our knowledge of the surface chemistry of most molecular solids remains completely unknown at this time. The surfaces of simple elemental compounds are known to reconstruct due to the termination of strong primary bonding at the exposed surface thus leading to relaxation of atoms from their bulk positions, resulting in surface symmetry reduction. Intuitively one would not expect such effects to be as strong in organic solids due to their crystal chemistry being dominated by much weaker van der Waals' forces. Despite this, recent molecular modelling studies by George *et al.*[1] have indicated the likelihood of a degree of surface re-ordering in molecular solids.

The inherent flexibility in many complex organic molecules would suggest that some molecular rearrangement should take place in cases where packing forces induce a change in molecular conformation with respect to that expected for the free molecule.[2]

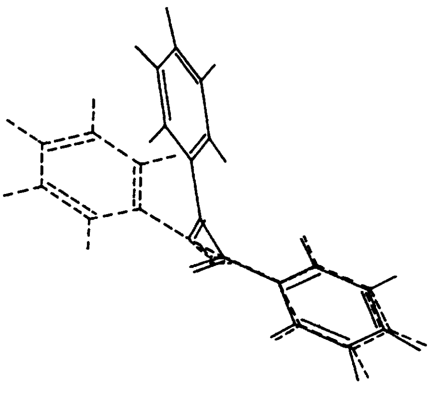

Fig. 1 Overlay of optimised (– – –) and crystallographically derived (——) molecular structures for benzil showing the nature of conformational changes induced by packing in the solid state

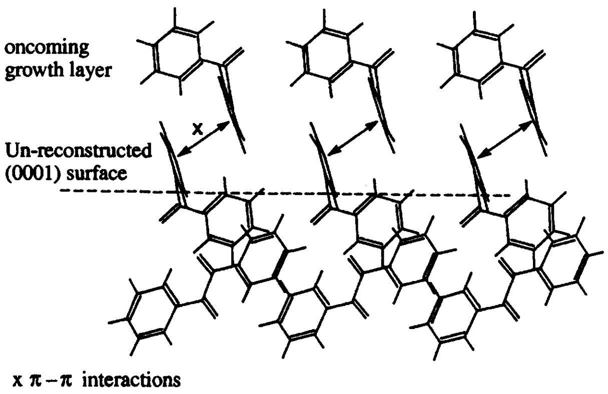

Fig. 2 Projection of the molecular packing onto the *a*-axis showing the interleaving intermolecular packing involved in the formation of the (0001) surface of benzil

Benzil $(C_6H_5C{=}O)_2$ comprises two phenyl rings joined together by two *trans* carbonyl groups, with the latter providing a degree of conformational flexibility. It crystallises in a trigonal structure $P3_12$ in a tri-molecular unit cell with $a = 8.409$ Å and $c = 13.672$ Å. Comparison between the molecular structure derived from semi-empirical quantum chemistry calculations† and that derived from the published crystallographic structure,[4] shown in Fig. 1, reveal a substantial change in molecular conformation reflected by the crystallisation process. This change, associated with an increase in the molar enthalpy of formation from 38.3 kcal mol^{-1} (1 cal = 4.184 J) for the isolated molecule to 97.5 kcal mol^{-1} for the same in the bulk crystal structure, reflects the strong intermolecular packing forces in the solid-state. These forces are dominated by an interleaved packing motif between benzil molecules from adjacent molecular layers which are, in turn, dominated by strong π–π interactions (as shown in Fig. 2) across the basal (0001) plane. It is the strength‡ of these π–π intermolecular interactions (−8.04 kcal mol^{-1}) with respect to the overall lattice energy (−25.9 kcal mol^{-1}) that maintain the benzil molecules in a conformation away from that expected for a minimum intramolecular energy.

It is thus reasonable to suppose that during the growth process the conformation of the benzil molecules on the (0001) surface will relax back towards that expected for the isolated

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† Calculations carried out using MNDO.[3]

‡ Calculations carried out using HABIT95[5] and Dreiding[6] force fields.

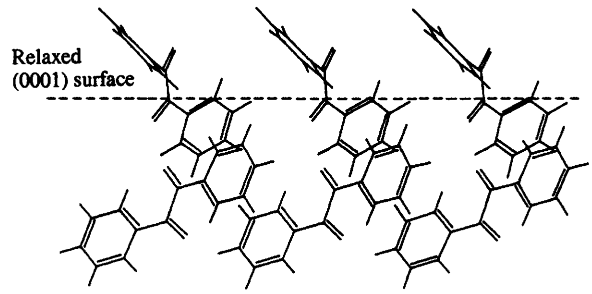

Fig. 3 Molecular diagram showing conformational change in the (0001) surface molecules following relaxation of the surface layer

molecular state. This supposition is confirmed (Fig. 3) through a detailed molecular minimisation study[§] carried out for benzil (0001). This reveals that the exposed surface molecules experience conformational change due to the loss of the intermolecular π–π interactions inherent in the bulk structure but missing on the exposed (0001) surface.

Experimental confirmation of this model is provided *via* the examination of single crystal samples[¶] using polarised ultra-soft X-ray absorption spectroscopy[8] at the carbon K-edge. The experiments were carried out on beamline U1A[9] at the national Synchrotron Light Source (NSLS) at Brookhaven National Laboratory in the USA. Absorption spectra were recorded at normal incidence (Fig. 4) simultaneously in electron yield and fluorescent yield modes. These techniques probe, respectively, 2 and 200 nm into the sample surface.[10] The fluorescence yield spectra, representative of the bulk crystal structure, reveal (*a*) well defined C–H*[8] and C=C π^*[11],[||] resonance features, together with other less distinct features. The strong C=C π^* resonance reflects the fact that the ring planes of the phenyl groups of the benzil molecules are aligned normal to the surface and hence the π orbitals of the molecules are parallel to the electric field vector of the linearly polarised synchrotron beam which for this orientation runs parallel to the sample surface. The C=C π^* resonance is substantially reduced in the electron yield data (*b*) reflecting significant disordering of the ring orientation in the phenyl rings in direct confirmation of the molecular modelling studies.

Thus in this work we have provided direct evidence for a degree of surface reconstruction in the organic solid-state. In the case of benzil (0001) the reconstruction involves conformational changes to the surface molecules, rather than shifts in their relative position, as would be more typical for such effects in elemental compounds. Studies are currently in hand with a view to assess how general these effects are in terms of organic solid state chemistry as well as to determine the role of molecular size, shape and bonding type on the surface reconstruction mechanism.

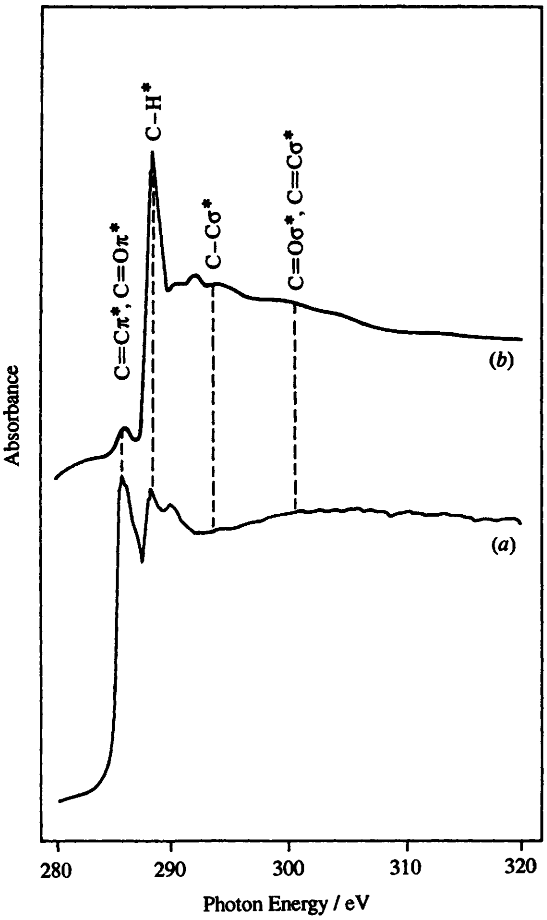

Fig. 4 Carbon K-edge X-ray absorption spectra recording in normal incidence from a Benzil 0001 surface in (*a*) fluorescence yield, (*b*) electron yield

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References

1 A. R. George, K. D. M. Harris, A. L. Rohl and D. H. Gay, *J. Mater. Chem.*, 1996, **5**, 133.
2 K. J. Roberts, R. Docherty, P. Bennema and L. A. Jetten, *J. Phys. D.: Applied Phys.*, 1991, **24**, 89.
3 M. J. S. Dewar, E. G. Zoebisch, E. F. Healy and J. J. P. Stewart, *J. Am. Chem. Soc.*, 1985, **107**, 3902.
4 E. J. Gabe, Y. Le Page, F. L. Lee and L. R. C. Barclay, *Acta Crystallogr., Sect. B*, 1981, **37**, 197.
5 G. Clydesdale, R. Docherty and K. J. Roberts, *J. Cryst. Growth*, in the press.
6 S. L. Mayo, B. D. Olafson and W. A. Goddard, *J. Phys. Chem.*, 1991, **95**, 2288.
7 R. Fletcher and C. M. Reeves, *Comput. J.*, 1964, **7**, 149.
8 J. Stohr and D. A. Outka, *Phys. Rev. B*, 1987, **36**, 7891.
9 M. Sansone, R. Hewitt, W. Eberhart and D. Sondericker, *Nucl. Instrum. Methods Phys. Res. A*, 1988, **A266**, 422.
10 D. A. Fischer, J. Colbert and J. L. Gland, *Review Sci. Instrum.*, 1989, **60**, 1596.
11 J. Stohr in *NEXAFS Spectroscopy*, Series in Surface Science 25, Springer, Heidelberg, 1992, 111.

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[§] For this calculation a co-ordinate minimisation using the conjugate gradient 200 algorithm[7] was used together with the Dreiding force field.[6]

[¶] Nearly perfect single crystal samples were prepared by crystallisation from the undercooled melt and cut into 0001 oriented plates (size *ca.* $5 \times 5 \times 1$ mm^3).

[||] The symbols π^* and σ^* are used in this text as a shorthand means of denoting an electronic transition from a core shell to an anti-bonding orbital. C–H* refers to transitions to both π^* and σ^* orbitals associated with the C–H bonds. These are conventions used by Stohr *et al.* in ref. 8 and also in the main text of Stohr's book, indicated in ref. 11 as well as by other researchers. However, in the particular context of Table 4.2, ref. 11, * is given an alternative use, this time to denote the excited atom.