

# Individual Grant Review GR/M94199/01

## First principles investigation of molecular crystals under pressure

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### Background

This was the researcher's first EPSRC grant and was obtained under the *fast track* scheme.

The intended outcome was to use first principles electronic structure calculation to investigate the structural properties of molecular crystals under pressure. A principal goal of the quantum mechanical simulations was the parameter-free determination of the molecular energy, electronic charge distribution, bond lengths and angles and the nature of bonding in materials. The motivation for performing these crystallographic studies on very simple systems is that they may reveal structural properties that are applicable to a whole class of compounds. This has been achieved for a variety of molecules and molecular crystals as described below. The work was also extended to a wider class of molecular materials including fluorinated phenols, metal-organics and liquid crystal forming molecules.

### Key Advances

To investigate the bonding interactions in molecular crystals, several different classes of materials have been studied so that a range of different bonding types can be explored. These include hydrogen-bonding, covalent systems, van der Waals/dispersion forces, electrostatics and metal-organic interactions. A brief summary of the major results and publications is given below.

#### 1. Organic Acids and Alcohols:

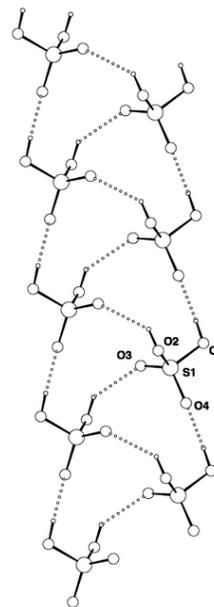
Publications: [1, 2, 3].

The effects of pressure on organic acids have been carried out both computationally, and the using x-ray diffraction in collaboration with Dr D Allan of the University of Edinburgh as outlined in the original proposal. The motive for performing such crystallographic studies such 'simple' systems is that they may reveal structural properties that are applicable to a whole class of compound. This continued our work on homologous series of organic acids (D. R. Allan and S. J. Clark, *Phys. Rev. Lett.*, 1999, **82**, 3464 and *Phys. Rev. B*, 1999, **60**, 6328).

Propionic Acid: The high-pressure crystal-structure of propionic acid was determined, including the calculated positions of the hydrogen atoms. This includes a previously unobserved triclinic P1 high-pressure. The relative phase stability was calculated using *ab initio* techniques between the new high pressure phase and the low-temperature monoclinic P2<sub>1</sub>/c phase. It was found that both are stable over a very narrow pressure range at just above

the ambient temperature crystallization pressure. Both structures were characterized by the formation of isolated dimers and the calculations indicate that the rearrangement of the molecules between the two structures results in a very small reduction in the enthalpy (0.062 eV/molecule) for the triclinic phase.

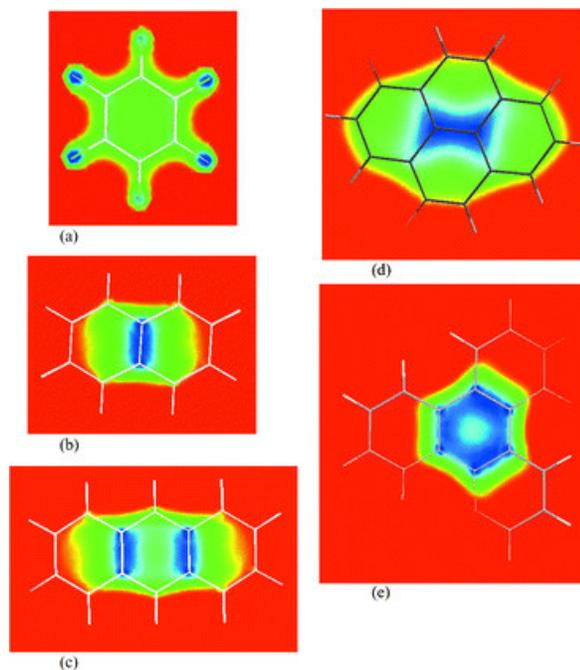
Sulphuric Acid: The high pressure and low temperature structures of sulphuric acid were determined and the phase stability calculated. The structure of the high-pressure monoclinic  $P2_1/c$  structure of sulfuric acid was calculated. This phase was previously unobserved and has a radically different hydrogen bonding topology to that observed in the low-temperature  $C2/c$  phase. The hydrogen bonding network was investigated by examination of atomic partial charges and the total electronic charge density and the phase behavior explained by a molecular packing arrangement that maximized the number of hydrogen-bonds per molecule as illustrated in the diagram.



## 2. Fluorinated Phenols:

Publications: [4, 5].

Perfluoroarenes, particularly hexafluorobenzene (HFB), are well-known to co-crystallise with arenes and derivatives, such as naphthalene, anthracene, phenanthrene, pyrene and triphenylene in the form of 1:1 molecular complexes, with nearly-parallel molecules stacked alternately in the solid state. The nature of intermolecular forces responsible for this was a subject of controversy; intermolecular charge transfer, van der Waals interactions, electrostatic interactions have all been proposed. In order to clarify this question *ab initio* calculations were performed to examine both geometric and electronic structures and propose a mechanism for binding in the crystalline form. Integrating the calculated electron charge density over each molecule in the unit cell, it was found that molecules of HFB as well as arenes in each of the complexes are neutral, hence eliminating molecular charge transfer. Thereupon the electrostatic energy was calculated directly, using the entire charge density distribution in the molecules (rather than atom-centred charges or multipole representations). Thus, in an important contrast to previous approaches, from the *ab initio* calculations used in the present work, there was no need to artificially assign partial charges to atoms. It was found that the electrostatic attraction contributes more than 90% of the total cohesion which is in contrast to previous theories which suggested a high proportion of van der Waals interactions were



prevalent in these co-crystals. Furthermore, to confirm the electrostatic nature of the interactions, the electrostatic potential was investigated as shown in the diagrams, where the electrostatic potentials of HFB, naphthalene, anthracene, phenanthrene, pyrene and triphenylene are shown. By comparing the regions of minimum potential in the co-crystals it was found that molecules in the stacks overlap in such a way as to maximise the distances between the minima of the electrostatic potential, *i.e.* the centres of the highest negative charge.

### 3. Intermolecular Interactions:

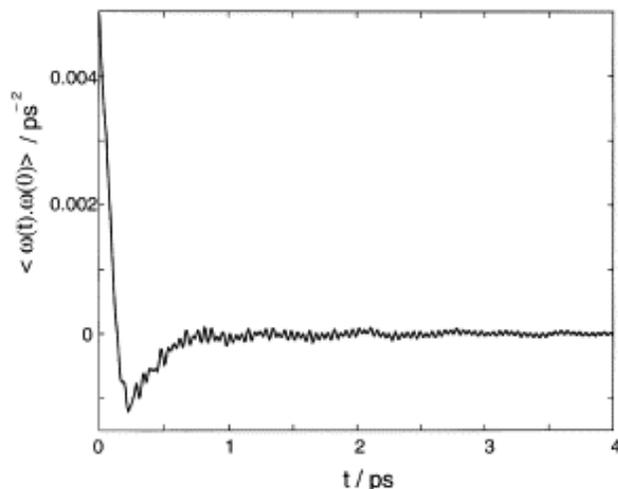
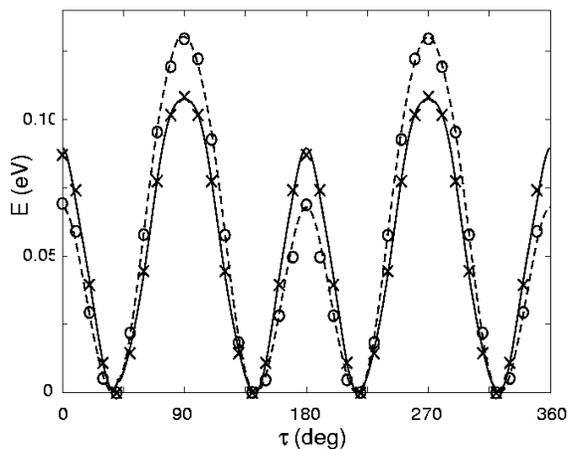
Publications: [6, 7].

Investigations have been carried out to study the form of both inter- and intra-molecular interactions in much more detail. It was decided that *ab initio* calculations could be used effectively in the parameterisation of atomistic potentials. These in turn could be used to calculate bulk properties of much more complex systems, for example bulk properties of liquid crystals. These systems were chosen because many of the early atomistic simulations of liquid crystals suffered from a poor description of both the intra and inter molecular interactions. Force fields to represent atomistic systems typically require terms to describe bond stretching, bond angle bending and internal rotations in addition to non-bonded interactions. The fully atomistic model which was represented by a harmonic force field of the AMBER form

$$E = E_{stretch} + E_{bend} + E_{torsion} + E_{vdW} + E_{Coulomb}$$

was parameterised from *ab initio* simulations. The force field parameters were found by fitting to potential energy surfaces of common liquid crystal components. These included biphenyls, with terminal cyano substitution and lateral fluorine substitutions, as well as other core components. Potentials for ring-tail torsions were calculated using propylbenzene. An example of the fit is shown in the figure for the potential of a torsional angle rotation in biphenyl (solid line) and cyanobiphenyl (dashed line). The lines show the fit and the symbols who the *ab initio* data. Here we can see a marked difference in the torsional potentials, caused by charge transfer toward the polar cyano group. This affects the bonding and structure in the molecule, changing the trade-off between steric repulsion and conjugation.

Equilibrium molecular dynamics calculations were performed for the liquid crystal molecule *n*-4-(*trans*-4-*n*-pentylcyclohexyl) benzonitrile (PCH5) using our. An exceptionally challenging test for such potentials is the evaluation of



rotational viscosities. This is an important parameter in determining the switching times of liquid crystal displays. The computed values of the system density and rotational correlation functions (the angular velocity correlation function for PCH5 at 310 K is shown in the figure) were in good agreement (within 2%) of the experimental values which gives a good indication of the accuracy of parameterised force field. This stringent test shows that the inter-atomic and inter-molecular interactions are obtained accurately from the *ab initio* calculations.

#### **4. Metal atom-organic interactions:**

Publications: [8].

This is work performed as part of a new collaboration with Dr N. Robertson, University of Edinburgh which was a result of the research described above and is a natural extension in describing the interactions in more complex systems.

Salts of  $[\text{Ni}(\text{dmit})_2]^{+}$  have been widely studied due to their ability to form molecular conductors and superconductors through the formation of intermolecular interactions in the crystalline phase combined with a flexibility in oxidation state that allows the partial band filling required for metal-like conductivity. Studies of such salts and those of related multi-sulfur organic species have involved systematic variation of the counter ions in order to change intermolecular interactions and hence the resultant conducting and magnetic properties. Owing to their unique structures, a series of *ab initio* calculations were performed where it was found that, unexpectedly, it was essentially an electrostatic interaction between the  $\text{M}^+$  and the di-anionic nickel complex with much negative partial charge residing on the central Ni and four coordinated S atoms.

#### **5. New *ab initio* methodologies**

Publications: [9].

Many of the results, above, are based on the evaluation of the total energy of the material, however derivatives of the total energy with respect to some perturbation often gives invaluable information regarding the properties of materials. Many experimentally determined quantities are responses of the total energy of the system, for example, derivatives on energy with respect to atomic position gives vibrational frequencies, derivatives with respect to applied electric field gives polarisabilities and permitivities, and magnetic fields give nuclear magnetic resonance chemical shifts. During the investigations, above, it became apparent that implementation of these responses would be an invaluable tool to further the research in inter-molecular interactions.

#### **6. Related work initiated due to the grant**

Some other work on molecular systems related to the current work was also performed using the grant. Details can be found in references [10, 11, 12].

## **Project Plan Review**

The initial objectives of this work was to

1. Use plane wave DFT methods to examine molecular crystals
2. Calculate their electronic and structural properties
3. Investigate the binding mechanisms in molecular crystals
4. Investigate the response of halide substituted molecular crystals
5. To investigate simple hydrides under pressure and examine more exotic forms of bonding

Each of these original objectives was achieved, although a detail of point 5 differs slightly. Complex bonding was investigated in metal-organic systems instead of the original hydrides originally proposed. The reason for this minor change was that it was advantageous to form a new collaboration with Dr N. Robertson by considering these systems.

In addition to this further work was performed by extending the methodologies used in investigating molecular crystals by implementing response techniques in the CASTEP code which is now freely available to all UK academics.

## **Research Impact and Benefits to Society**

This research has provided an insight into the properties of fundamental molecular systems, which has been relevance to a wide range of groups studying molecular crystals, liquid crystals and metal-organic complexes. One of the main aims of the work was to obtain accurate structural information, and in particular the position of hydrogen atoms in these materials. This has been successfully achieved and, with continued collaboration with experimental colleagues, is proving to be of great importance in structure determination of molecular systems. This has been of particular relevance to Dr D. R. Allan of the Department of Physics, University of Edinburgh. There is also experimental groups in the Department of Chemistry, Universities of Edinburgh and Durham run by Dr. C. Pulham, Dr. S. Parsons, Dr N. Robertson and Prof. T Marder who have benefited (and continue to benefit) from the structural details obtained in this work, all of whom have an interest in the structure of molecules within the solid state.

In addition to this, all new *ab initio* techniques used under this grant have been implemented in the CASTEP code which can be obtained freely by any UK academic.

## **Explanation of Expenditure**

The main use of the grant was to cover the costs of the fees and subsistence of a PhD student. Unfortunately, the student originally employed on the grant had to leave after one year to return home to Italy due to personal reasons (family illness). A second student was employed with remaining funds and the shortfall made up from departmental funds. He is now in his 3<sup>rd</sup> year of study and will complete his PhD in October 2004.

All other funds were spent as stated in the original grant proposal; 4% of time for a computing officer, computer equipment on which the calculations were performed, and travel/subsistence to conferences at which the results were presented.

## Further Research

The excellent results obtained under the grant have opened up many possibilities for future work. As noted above, it instigated further development of *ab initio* methods in the area responses of total energy to external perturbation. Several of these methods have now been implemented and others are now planned.

In addition to this, the work in inter-molecular interactions has initiated new collaborations with other researchers including Dr. N Robertson in the University of Edinburgh where work is continuing in the investigation of the interaction of metal atoms in organic systems. A new collaboration has also been formed with Prof. T Marder of the University of Durham where the role of fluorine substitution in phenyl compounds is being investigated and the nature of the inter-molecular binding is being questioned.

## Publications resulting from the grant

1. D. R. Allan, **S. J. Clark**, S. Parsons and M. Ruf "A high pressure study of propionic acid", *J. Phys. Condens. Mat.* **12** L613 (2001).
2. D. R. Allan, **S. J. Clark**, A. Dawson, P. A. McGerger and S. Parsons "Comparison of the high-pressure and low-temperature structures of sulfuric acid", *J. Chem. Soc. Dalton* **8** 1867 (2002).
3. D. R. Allan, **S. J. Clark**, A. Dawson, P. A. McGregor and S. Parsons, "Pressure-induced polymorphism in phenol", *Acta Cryst. B* **58** 1018 (2002).
4. J. C. Collings, K. P. Roscoe, E. G. Robins, A. S. Batsanov, J. A. K. Howard, **S. J. Clark** and T. B. Marder, "Arene-perfluoroarene interactions in crystal engineering 8: structures of 1:1 complexes of hexafluorobenzene with fused-ring polyaromatic hydrocarbons", *New J. of Chemistry* **26**, 1740 (2002).
5. C. E. Smith, P. S. Smith, R. L. Thomas, E. G. Robins, J. C. Collins, A. J. Scott, S. Borwick, A. S. Balsanov, S. Watt, **S. J. Clark**, J. Howard, W. Clegg and T. Marder, "Structural preferences in polyfluorinated tolans", *J. Mat. Chem*, in press, (2004).
6. D. L. Cheung, **S. J. Clark** and M. R. Wilson "Calculation of the rotational viscosity of a nematic liquid crystal", *Chem. Phys. Lett.* **356** 140 (2002).
7. D. L. G. Cheung, **S. J. Clark** and M. R. Wilson "Parametrization and validation of a force field for liquid-crystal forming molecules", *Phys. Rev. E* **65** 051709 (2002).
8. L. Cronin, **S. J. Clark**, S. Parsons, T. Nakamura and N. Robertson, "Unique structural topologies involving metal-metal and metal-sulphur interactions", *J. Chem. Soc. Dalton*, **8** 1347 (2001).
9. M. D. Segall, P. J. D. Lindan, M. J. Probert, C. J. Hasnip, **S. J. Clark** and M. C. Payne "First-principles simulation: ideas, illustrations and the CASTEP code", *J. Phys. Condens. Matter* **14** 2717 (2002).
10. E. M. King, **S. J. Clark**, C. F. Verdozzi and G. J. Ackland "Interaction between metallic *p*-orbitals and the  $\pi$ -orbitals of organic molecules", *J. Phys. Chem. B* **105**, 641 (2001).
11. D. Bloor, Y. Kagawa, M. Szablewski, M. Ravi, **S. J. Clark**, G. H. Cross, L. O. Palsson, A. Beeby, C. Parmer and G. Rumbles "Matrix dependence of light emission from TCNQ adducts", *J. Materials Chem.* **11** 3053 (2001).
12. **S. J. Clark** and G. J. Ackland "*Ab initio* molecular dynamics of liquid carbon disulphide", *Mol. Phys.* **99** 855 (2001).