Title of Case Study: Observing the formation of a chemical bond

Grant Reference Number or Facility Name: Nottingham Trent University accessing National Crystallography Service, University of Southampton

One sentence summary: Novel research involving Southampton's National Crystallography Service (NCS) is using newly developed solid-state NMR techniques combined with ultra-high resolution single crystal X-ray diffraction to enable chemists to 'see' how a chemical bond is formed.

One paragraph summary:

Using high-resolution quantum crystallography, results from the NCS are supporting research from Nottingham Trent University and the University of Warwick to monitor the different stages of a chemical reaction i.e. the formation of a chemical bond. Quantum crystallography approaches can measure the electron density and compute key properties that act as a gauge for bonding behaviour. These results are correlated with those from Solid-State NMR at the University of Warwick and enabled the parameterising and benchmarking of entirely new methods to follow this kind of behaviour.

Key outputs in bullet points:

Data generated at NCS is enabling:

- Use of high-powered diffractometers to study bond critical point formation in a series of naphthalene compounds
- A crystallographic comparison to solid state NMR and DFT calculations to provide a more complete picture of this bond formation and benchmark new NMR methods
- Nottingham Trent, Southampton & Warwick universities to published in high quality journals (Angewandte Chemie) and for data to be combined from several technique in order for the research to be progressed to it's full potential

Main body text

Using high-resolution quantum crystallography, results from the NCS are supporting research from Nottingham Trent University and the University of Warwick to monitor the different stages of a chemical reaction i.e. the formation of a chemical bond. A range of related compounds where the core of the molecule remains the same and exhibits an intramolecular interaction have been synthesised and crystallised. Each molecule has a different functional group that withdraws or donates electrons into the interaction and so the series represents the different stages of bond formation as a greater number of electrons are made available for sharing. Quantum crystallography approaches can measure the electron density and compute key properties that act as a gauge for bonding behaviour. These results are correlated with those from Solid-State NMR at the University of Warwick and enabled the parameterising and benchmarking of entirely new methods to follow this kind of behaviour.

This high-resolution quantum crystallography technique has never before been used to systematically look at a bond being formed, and is a collaboration between the universities of Southampton, Nottingham Trent and Warwick. The impact of their work has recently been recognised with a paper being published in the prestigious chemistry journal Angewandte Chemie as a 'Hot Paper' (one of its top 10 per cent most important papers).

Professor Simon Coles, Director of NCS, led Southampton's contribution to the work. He says: "This research is about being able to 'see' how a chemical bond forms, which you can't do with many experimental techniques. The only way to do this at a resolution that allows you to 'see' the electrons involved, is in a crystal. This high-resolution single crystal X-ray diffraction allows us to look at maps of where the electrons are, rather than the more traditional 'balls and sticks' that we are used to seeing in molecular structures."

Professor John Wallis, from Nottingham Trent University, masterminded the synthesis of novel molecules suitable for this study. By adding different functional groups to one of two interacting (but not bonded) atomic centres, the level of interaction between the two atoms could be tuned to see one atom increasingly ‘reaching out’ to the other to form a bond.

The University of Warwick group, led by Professor John Hanna, performed solid-state NMR experiments, a technique that can detect non-bonded interactions between atoms, and developed a cutting-edge new approach based on double isotopic labelling that can be applied to many different areas.

Simon says the results of the research provide a fundamental understanding of how much difference a chemical change actually makes when ‘adding electrons’ and gives insight into a whole range of different types of chemistry involving intermolecular interactions.

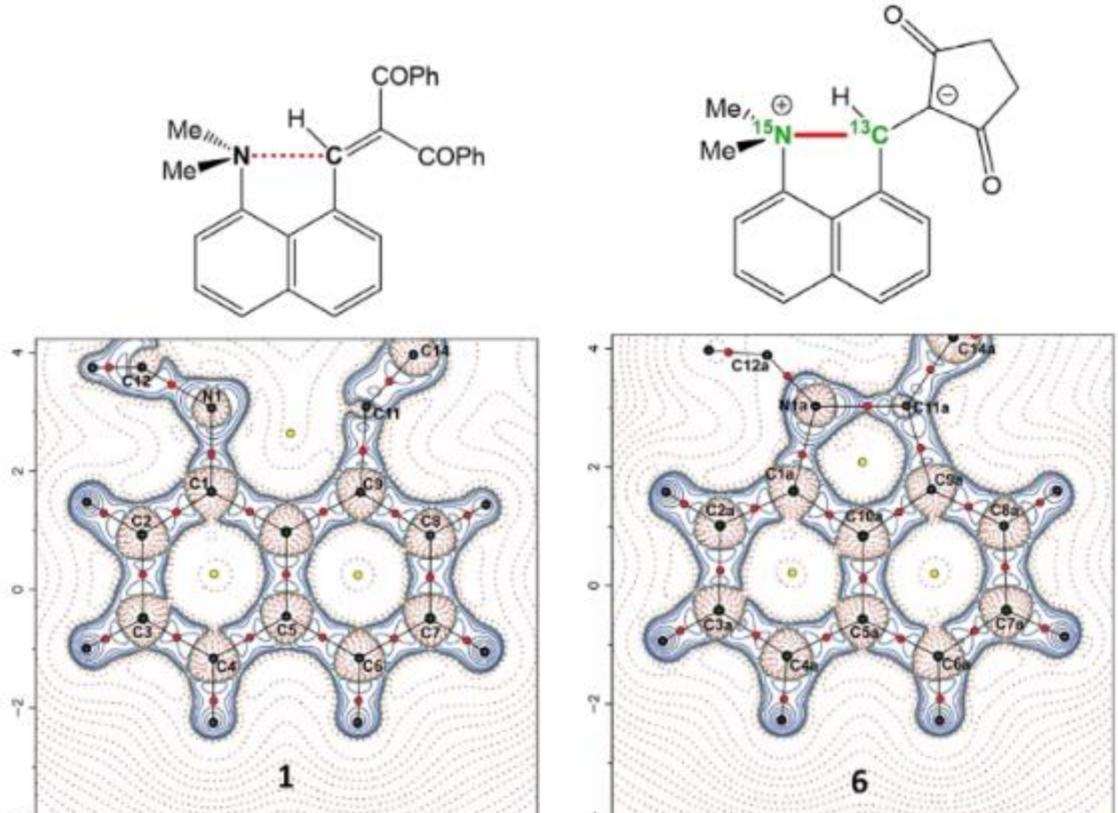

Figure 1. Demonstration of different electron density distributions between the peri-substituted groups on a naphthalene core

He adds: “For a chemist to be able to ‘see’ a chemical bond being formed is truly exciting and provides a fundamental understanding of our subject. Being able to ‘tune’ a system to control whether a bond forms or not gives much more control over chemical synthesis and even more over chemical reactivity.”

The NCS was involved in the high-resolution X-ray diffraction part of the research and Simon says the work is a testament to the skills and capabilities of the NCS and its staff.

“We are looking to include these advanced techniques as part of our service offering from next year, so this gives us some kudos and is a great example to the wider chemistry community of what we can do,” he says.

The research builds on work by the three universities that started more than a decade ago and involved the University of Southampton's current President and Vice-Chancellor Professor Mark E Smith. Mark at that time led the University of Warwick's Solid State NMR group and was a Principal Investigator on the original EPSRC-funded project.

Names of key academics and any collaborators:

Prof John Wallis (Nottingham Trent University)

Prof John Hanna (University of Warwick)

Prof Simon Coles (University of Southampton)

Sources of significant sponsorship (if applicable):

EPSRC Physical Sciences Initiative (EP/E018203/1) funded the initial idea.

EPSRC funds the National Crystallography Service (contract PR150005).

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The University of Warwick Scientific Computing Research Technology Platform (RTP), and EPSRC grant EP/K000128/1, for access to the TINUS and MINERVA high-performance computing clusters.

Who should we contact for more information?

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