

Single Crystal to Single Crystal Transformations

Leonard J. Barbour^A

^A Department of Chemistry, University of Stellenbosch, 7602 Stellenbosch, South Africa. Email: ljb@sun.ac.za

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The past decade has witnessed escalating interest in solid-state phase transitions that involve significant changes in structure without appreciable loss of crystal mosaicity—single crystal to single crystal (SC-SC) transformation.^[1–5] Several factors have contributed to these studies: increased general access to X-ray diffraction facilities, software-assisted demystification of crystallography, technological developments leading to rapid intensity data collection, and the popularization of crystal engineering as a research field. The two most active areas of interest with regard to SC-SC transformations are the development of porous materials and solventless topochemical reactions. Recent new results representing the current state-of-the-art with regard to both of these topics are reported in the Research Front of this issue of the *Australian Journal of Chemistry*.

In 1988 Dunitz, Schomaker, and Trueblood recounted a prior statement by Nobel Laureate (chemistry, 1939) Leopold Ruzicka, that ‘a crystal is a chemical cemetery’. This was interpreted to imply that, in sharp contrast to liquids and gases, the solid state consists of molecules that are lifelessly interred in fixed geometrical arrangements with little prospect of an interesting existence.^[6] However, it has long been known that structural rearrangement can occur in the solid state in response to a variety of physical or chemical factors. Provided that these structural changes are subtle, it is reasonable to expect that the relative absence of mechanical stress would allow individual crystals to retain their mosaicity, both during and after transformation. In most cases, though, changes of the chemical composition and/or molecular conformation and/or packing arrangement within crystals are well known to cause catastrophic disruption of packing continuity. Concomitant fracturing of

the once pristine material occurs to yield countless microcrystalline particles—any crystallographer who has manipulated crystals that lose lattice-included solvent molecules under atmospheric conditions knows this all too well.

The deliberate construction of porous crystalline materials with a view to mimicking or even surpassing the fascinating and useful properties of zeolites has recently become a highly attractive area of research.^[7] One of the most common strategies involves the formation of solvent-templated frameworks, followed by facile removal of the solvent guest molecules with retention of the host framework structure as a porous matrix. Extended metal–organic host frameworks (MOFs) are particularly attractive in this regard because of the intrinsic long-range rigidity of metal centres (with their well-defined coordination geometries) interconnected by bridging ligands.^[8] This concept is nicely illustrated by Zheming Wang, Mohamedally Kurmoo, and co-workers^[9] who describe a simple diamondoid zinc-centered ZnZn_4 framework, based on formic acid linkages, which includes methanol and water molecules. The guest molecules can be removed to afford an empty, porous structure which can then absorb and desorb a range of solvent molecules as well as gases, all the while retaining the mosaicity of the crystals. The host framework has the ability to adjust its geometry slightly in order to conform to the different guests. Myunghyun Paik Suh and Young Eun Cheon have also prepared several MOFs that undergo SC-SC transformations upon guest removal, uptake, and exchange as well as chemical oxidation.^[10] In some cases, significant rearrangement of the molecular components is observed, including shrinking and swelling as well as sliding, swinging, bending, and rotational motion, all without loss of single crystallinity. Interestingly, guest-dependent



Len Barbour was born in Pretoria, South Africa, in 1965. In 1994 he obtained his Ph.D. under the supervision of Luigi Nassimbeni at the University of Cape Town where he investigated thermodynamic and structural aspects of solvate formation and decomposition. He then undertook a postdoctoral fellowship with Jerry Atwood at the University of Missouri-Columbia where he continued to pursue his interest in supramolecular chemistry and where in 1997 he was appointed as Research Assistant Professor. In 2003 he moved back to South Africa to the University of Stellenbosch. He was promoted to Professor of Chemistry in 2005 and currently holds a South African Research Chair in Nanostructured Functional Materials. His research interests include the study of solid-state phenomena with particular emphasis on the design and characterization of porous materials for gas sorption.

absorption and luminescence are also observed, although a rational explanation for these phenomena cannot as yet be advanced. For a broader overview of SC-SC transformations in hydrogen bonded, as well as rigid and flexible coordination framework materials, the reader is referred to the informative short review by Gregory Halder and Cameron Kepert.^[11]

The concept of carrying out [2+2] photodimerization of alkenes in the solid state was pioneered more than 30 years ago. However, Len MacGillivray and Tomislav Friščić have advanced this work significantly by applying rational design strategies based upon the use of linear templates in order to control the placement of C=C double bonds. Over the past few years they have achieved remarkable success with a variety of templates and in this issue they describe the formation of an intermediate product in a two-step solid-state synthesis of a [2.2]paracyclophane.^[12] Despite changes in the overall shape of the molecular assembly as a result of chemical reactions, monocrystallinity is maintained throughout the process.

Many potential applications that involve solid-state dynamics (for example catalysis, gas storage and separation, or topochemical reactions) do not require retention of mosaicity. However, the phenomenon of SC-SC transformation is important for the following reasons:

- (a) rationalizing how molecules in confined spaces cooperate with one another in a concerted fashion to effect stress-free structural modifications presents a fascinating scientific challenge;
- (b) when such changes occur, it is possible to use the immensely powerful analytical tool of single-crystal X-ray diffraction in order to structurally characterize both the initial and final phases; and
- (c) for a crystal is to be incorporated into a device such as a substrate-triggered sensor or actuator, monocrystallinity would be essential for repeated operation.

Taken together, the studies described in this Research Front patently illustrate that the classical perception of crystals as chemical cemeteries is grossly flawed—it is abundantly clear that a significant degree of dynamic behaviour occurs in the solid state. This phenomenon is even more surprising when large changes occur within the crystal without

loss of mosaicity.^[13] Because crystals are intrinsically brittle, conventional wisdom dictates that mechanical stress will occur if the molecules change shape or rearrange unless they cooperate with one another. To date, the phenomenon has been considered rather rare because the manipulation of structure has only recently begun to receive significant attention. However, it is my opinion that it is not as rare as one might think and I confidently predict that many additional systems will be found to undergo SC-SC rearrangements as solid-state chemists become more attuned to investigating and recognizing such properties. The challenge for the future is to understand how the solid state can exhibit such astonishing fluidity while maintaining its structural integrity, and then to harness the phenomenon.

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