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Dynamic behaviour and reactivity in crystalline solids

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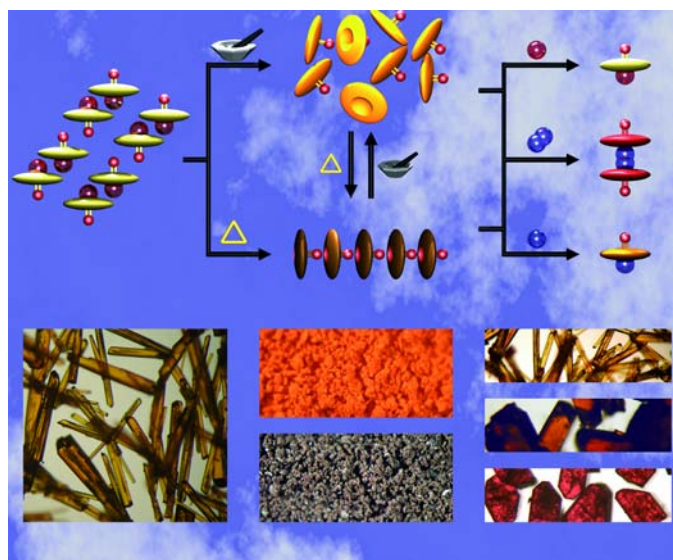


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EDITORIAL

Crystal engineering: origins, early adventures and some current trends

Sir John Meurig Thomas*

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Anyone who is merely vaguely interested in the topic of crystal engineering is aware that, in the 1960s, Schmidt and Cohen at the Weizmann Institute of Science, were the giants in this field. Along with other advances, they pioneered the notion that the photoreactivity of certain organic molecules in the solid state was governed more by their immediate stereochemical vicinity than by their intrinsic electronic properties. They also showed that it was possible to effect absolute asymmetric syntheses in the solid state, under abiotic conditions, from optically inactive materials, by inducing solid-state or surface reactions in chiral crystals.

Occasionally, however, their predictions and expectations as to which product would be formed within a crystal subjected to photoirradiation turned out to be wrong. 9-cyanoanthracene was a case in point. Instead of forming the *cis* dimer of the diparaanthracene, the *trans* dimer appeared on irradiating crystals of the monomer, in which molecules were stacked in columns with “incipient *cis*” orientation. This and other examples proved enigmatic.

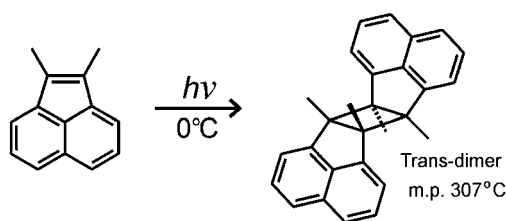
In the 1960s, my students and I at Bangor had found that dislocations in crystalline solids often exerted a profound influence on the reactivity of both inorganic and organic materials. Two particular examples were the thermally-stimulated decomposition of calcite (CaCO_3)¹ and the photodimerization of anthracene.² My work led Cohen and Schmidt to invite me to their laboratory in 1969, to lecture on crystalline defects and to do joint research there, all focused on the chemical consequences of imperfections in solids. One of

the consequences was the discovery that acenaphthylene (Scheme 1), under irradiation with 300 nm light, dimerized preferentially at dislocation cores.³

Upon my translation from Bangor to Aberystwyth in 1969, I embarked on a systematic study of how imperfections of one kind or another in organic molecular crystals influenced their excitonic, electronic, photo-physical and photo-chemical behaviour. With Cohen and the late J. O. Williams, we showed how the *trans* dimer of 9-cyanoanthracene could be formed preferentially at stacking faults within the crystal (Figure 1).⁴ We also showed⁵ that excitons, from measurements of their life-

times as well as prompt and delayed fluorescence, could be used to probe the energetics of structural imperfections in crystalline anthracene. By the time Bill Jones had finished his PhD at Aberystwyth in 1974, he was an expert in the electron microscopy of beam-sensitive materials, a skill which he now utilizes in his pioneering investigations of pharmaceutical materials.⁶ He mastered dislocation theory and, *inter alia*, he discovered the ease with which certain organic molecular crystals underwent martensitic transformations.⁷

In 1974, having delved into what had been the early pioneering work of Kohlschütter in Germany and



Scheme 1 Solid-state photodimerization of acenaphthylene.³

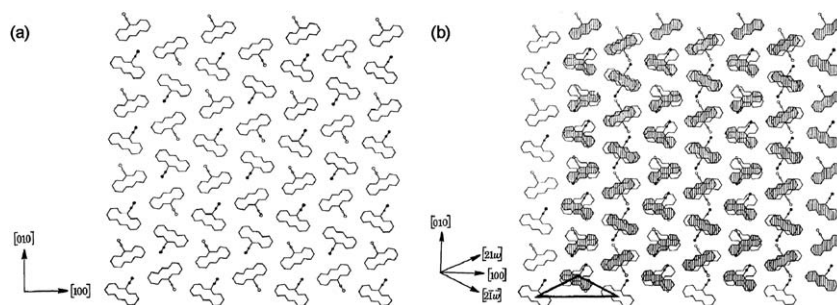


Fig. 1 Schematic illustration of (a) the ideal structure of 9-cyanoanthracene projected onto the (001) plane and (b) the nature of the stacking fault that leads to the formation of centrosymmetric dimers in the crystals of 9-cyanoanthracene. This image has been reproduced by permission of the Royal Society.⁴

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Kitaigorodsky in the Soviet Union, I opted, when invited by the Royal Society to present a review lecture, to talk on topography and topology in solid-state chemistry.⁸ This drew my attention to the work of Hasegawa *et al.* in Japan and Wegner *et al.* in Germany, each on photopolymerization within organic crystals, the former in 2,5-distyrylpyrazine (DSP) (Figure 2), the latter in substituted diacetylene monomers (Figure 3). This review also enabled me to explain, *inter alia*, the distinction between topochemical and topotactic reactions. It also had the added bonus of attracting one of Hasegawa's associates, Hachiro Nakanishi, to join Bill Jones and me, when I moved to Cambridge in the late 1970s.

Progress in organic solid state chemistry at the Department of Physical Chemistry, Cambridge in the subsequent years proved rewarding. We were able to determine, by a combination of low-temperature electron microscopy and atom-atom potentials, which Kitaigorodsky had been using some decades earlier, that Simonetta in Milan had refined, in a sophisticated manner, the crystal structure of a metastable phase of

anthracene and to predict its phonon spectrum (which was later confirmed experimentally).¹⁰ A baffling observation, the fact that crystals of hexahelicene (space group $P2_12_12_1$) display very little optical activity, also yielded to our studies. Atom-atom potentials enabled us to explain why this is so. The crystals contain recurrent intergrowths of the right and left-handed regions,¹¹ it was not homochiral. The atom-atom approach also enabled the determination, with the aid of low-temperature electron diffraction by selected area studies in electron microscopy, of the structure of a new phase of pyrene.¹²

With Nakanishi, Bill Jones and I were fortunate to unearth a rich vein of related organic monomers, based on 2-benzyl-5-benzylidenecyclopentanones (Figure 4). The delicate interdependence of the crystal structure and reactivity in this family of related molecules, derived by various substitutions for X, Y and Z in the rings A, B and C, could be carefully traced.¹³ One of the most satisfying consequences of this facet of our work was that we could genuinely engineer organic crystals so as to

control the photoreactivity of the reactants and crystallinity of the products.¹⁴ Moreover, not only could comparisons be made between the various substituents (*e.g.* chloro and methyl groups) in steering the engineering process towards desirable photoactive reactants,^{15,16} we were also able to track, with M. B. Hursthouse, the subtle atomic displacements associated with the conversion of two juxtaposed monomers into a dimer occupying essentially the same volume as the original pair of monomers.¹⁷

The topic of crystal engineering is still flourishing: it is, in effect, the rational design of functional molecular solids and it has received voluminous attention. The literature up until 1988 was summarized and addressed in the monograph by Desiraju,¹⁸ who has more recently¹⁹ reviewed the subject and many of its myriad ramifications up to 2007. One facet of this vast subject, which continues to elicit much attention, devolves upon the importance of co-crystallization.

Co-crystallization was used²⁰ by this author as a stratagem to bury molecules of H_2O_2 in a readily soluble solid so as to be able to release the peroxide on demand for use as a bleaching agent.²⁰ It was the large number of weak hydrogen bonds involving $\text{N-H}\cdots\text{O}$ and $\text{O-H}\cdots\text{O}$ that would be formed between the guanidinium oxalate dihydrate host and the H_2O_2 guest that constituted the element of crystal engineering, in my thinking.

In the recent work of Jones *et al.*, which focused on cocrystal architecture and the occurrence of chiral and racemic structures²¹ and cognate topics, terahertz (*i.e.* far infrared) time-domain spectroscopy has been used²² to probe cocrystal formation, leading to worthwhile insights.²³ One very powerful recent technique involving chiral crystals, which could offer penetrating insights into the mechanism of (*in situ*) co-crystal formation, is that of vibrational optical activity, pioneered and recently reviewed by Barron and Buckingham.²⁴

It is invidious for anyone, like me, who is no longer active in the field of crystal engineering, to predict possible future developments; but it is surely uncontentious to remark that such is the rapidity with which the structures of solids may now be retrieved from both single-crystal and powdered²⁵ specimens, that it is the arrival of yet far more powerful techniques²⁶ for *in situ* studies of

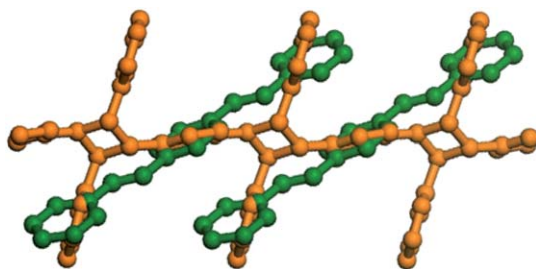


Fig. 2 Overlay of two molecules in the crystal of 2,5-distyrylpyrazine (green), with the polymer resulting from their solid-state [2 + 2] photopolymerization (orange). This image has been reproduced by permission of the American Chemical Society.⁹

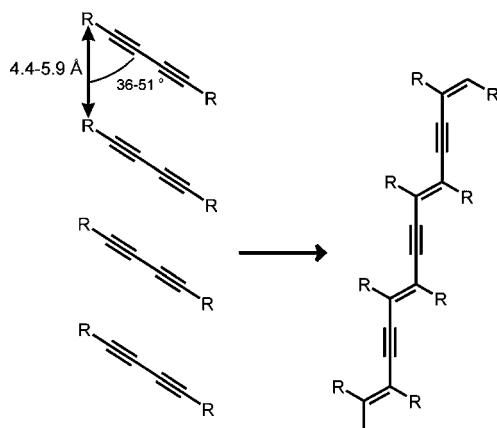


Fig. 3 Topochemical polymerization of a diacetylene.

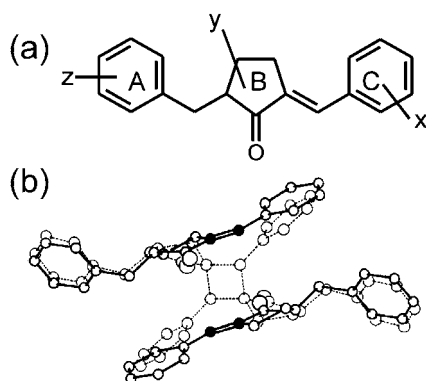


Fig. 4 (a) Schematic diagram of a 2-benzyl-5-benzylidenecyclopentanone molecule and (b) the two neighbouring molecules of its monomer in the crystal (in which bonds are drawn with full lines) compared to the molecule of the dimer (in which bonds are drawn with dotted lines), which is generated from them when the crystal is exposed to ultraviolet radiation.

crystallization (and co-crystallization) that may hold the key to deeper understanding in future investigations.²⁷ So far as the dynamics of change in organic crystalline solids is concerned, there will doubtless be major advances made, especially for those molecular crystals that are not too vulnerable to electron-beam damage, from the application of 4-D electron microscopy (4DEM), where time-resolution of femtoseconds to the bond-breaking and bond-making durations are possible.^{28,29} Other exciting prospects may emerge from the dramatic success recently reported^{30,31} from Stanford, whereby femtosecond X-ray protein nanocrystallography is described using the free-electron X-ray laser. One of the penalties that has to be paid in the X-ray laser work is that the crystal under study is destroyed almost immediately after it yields its diffraction pattern! There is no doubt that 4DEM and X-ray laser crystallography together will, and already have, enormously increase our knowledge of the dynamics of change in the solid state.

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