Crystal porosity and the burden of proof†

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The study of porosity in the context of crystal engineering is rapidly growing in intensity. However, claims of porosity are often highly subjective and use of the term ''porous'' is susceptible to abuse. This contribution discusses some of the criteria to be considered when stating that a particular crystal structure is porous.

Introduction

If you mentioned porous crystals as recently as ten years ago, you would most likely have been alluding to zeolites,[1] the well-known open-framework aluminosilicate hosts that are permeable to small guest molecules. With a global annual market of several million tons, zeolites have been used with phenomenal success in a variety of applications. Major uses include petrochemical cracking, ion-exchange (water softening and purification), and the separation and extraction of gases and solvents. Other applications are in construction, agriculture and animal husbandry. Although most zeolites occur naturally as minerals, significant effort has also been devoted to the production of synthetic zeolites with tailored properties. Since aluminosilicates form highly rigid scaffolds, zeolite frameworks generally do not collapse when their guest molecules are removed to thus yield robust materials with vacant networks of interconnected channels and cavities. Little wonder then that emulation of this intriguing phenomenon is currently one of the foremost goals of crystal engineers.

At this juncture it should be clearly stated that conventional porosity functions at the molecular scale and thus requires the presence of infinite channels with a minimum diameter of about 3 Å (typically 3 to 10 Å) in the skeletal host framework.[1] It is widely understood that molecules in crystals tend to pack as close to one another as possible in order to maximise attractive intermolecular contacts. Therefore it is quite rare to encounter molecular crystals with open channels, or with discrete lattice voids larger than about 25 $Å^3$.[2] For this reason, molecular crystals have generally not received much attention from researchers aiming to produce porous materials as functional analogues of zeolites. However, coordination polymers (metal–organic frameworks, or MOFs) are far more attractive in this regard because, like zeolites, they consist of effectively infinite frameworks of interconnected structural units.[3] These frameworks are based on the well-defined coordination geometries around metal centres, so the structural permutations accessible by combining a vast array of metal ions with various anions and bridging ligands are practically limitless.[4] In many cases, solvent molecules fill the gaps formed by the metal–ligand networks and a growing number of these systems are being shown to possess the rigidity necessary to survive evacuation to yield robust porous structures.

Several research groups currently concentrate all their efforts on the study of porosity in crystals and some recent high-profile successes[5] have undoubtedly stimulated significant additional interest in this area. Furthermore, the much fêted ''Hydrogen Economy'' has made a highly publicised appeal for novel materials capable of controlled uptake and release of hydrogen gas in technologically relevant quantities for stationary, mobile and portable applications.[6] As a result, crystal chemists are now far more attuned to recognising porosity (or the potential thereof) in crystals, whether obtained by serendipity or design. However, owing to the rather sudden recent focus on porous materials, it appears that the question of exactly what constitutes porosity is open to a significant degree of interpretation. A review of the literature dealing with porosity shows that the phenomenon can be classified

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into three distinct categories: conventional porosity, porosity "without pores" and virtual porosity. Before discussing these in turn, it is of practical use to postulate a functional definition of crystal porosity, but without involving a legal team. Indeed, the importance and flexibility of such definitions within a particular research niche was eloquently discussed by Joel Bernstein in a recent article in this series.[7] In this context it seems reasonable to suggest a simple, yet useful definition of porosity based upon two key aspects, each of which carries with it the burden of proof:

(1) Permeability should be demonstrated because the words "permeable" and "porous" are practically synonymous;[8]

(2) In order to be meaningful, the term "porous" should apply to a specific host phase and not simply to the host molecules as an amorphous or mutating collective. Therefore, in principle, the host framework should remain *substantially unaffected* by guest uptake and removal. Of course atomic coordinates and unit cell parameters of crystals are by their very nature given to numeric uncertainty and hence the term "substantially unaffected" is inescapably subjective. Consequently, any suggestion of porosity needs to be supported by a narrative aimed at convincing the audience that framework integrity is preserved *in principle*. Although unanimous accord is likely to be reached in the overriding majority of cases, it is inevitable that some instances will elicit disagreement and debate.

Virtual porosity

Virtual porosity can take various forms and is the easiest kind to create. This most often involves deleting selected atoms (usual candidates include small counterions, solvent molecules and sometimes even the ligands bridging two metal ions!) from a file containing the asymmetric unit of a crystal structure. Then a packing diagram is generated to show that large open channels have been fabricated by this process. Astonishingly, it is then claimed that the channels thus generated are pores. The decision of which molecules to delete is usually based not on their real ability to diffuse through the crystal, but on the category into which we subjectively place them (*e.g.* a molecule that we choose to define as a guest, regardless of whether or not it plays a pivotal structural role). Such claims of porosity are usually not supported by a demonstration that the host frameworks are indeed permeable and that they can survive guest removal *in situ* as readily as they do *in silico*.

Another form of virtual porosity entails the use of capped-stick or ball-and-stick plots in figures. Although such representations provide a clearer view of atomic connectivity than do space filling diagrams, they are misleading metaphors in terms of the volume occupied by atoms. For example, Fig. 1a shows two L-shaped molecules that associate in the solid state to form a rectangular dimer. The measurements shown imply that the rectangle encloses a "cavity" of dimensions 9.5 × 3.9 Å, and since adjacent rectangles are stacked one above the other, a tubular extended structure results. However, a space filling diagram (Fig. 1b) rendered to the same scale reveals immediately that there is no atomic-scale void space within the dimeric rectangle, and at best, the overall structure should be described as "columnar".

Where virtual porosity is concerned, the obvious danger is that some authors, in their enthusiasm to create a favourable impression of their work in a fashionable niche area, are making misleading statements and are thereby demeaning the remarkable phenomenon of crystal porosity. The examples described above are taken from recent articles published in respected journals. However, these papers are intentionally not cited here since the primary purpose of this contribution is to constructively raise awareness of the possible pitfalls associated with unrealistic claims of porosity. Here I would like to emphasise that most authors clearly appreciate that porosity involves permeability without structural collapse and reports of virtual porosity are thankfully rare.

Porosity "without pores"

In contemplating the category of porosity "without pores" it seems absurd to suggest that crystals possessing lattice voids, but no atomic-scale channels leading to these voids, might be permeable. For example, when sublimed at 270 °C under vacuum, the bowl-shaped molecule *p*-*tert*-butylcalix[4]arene

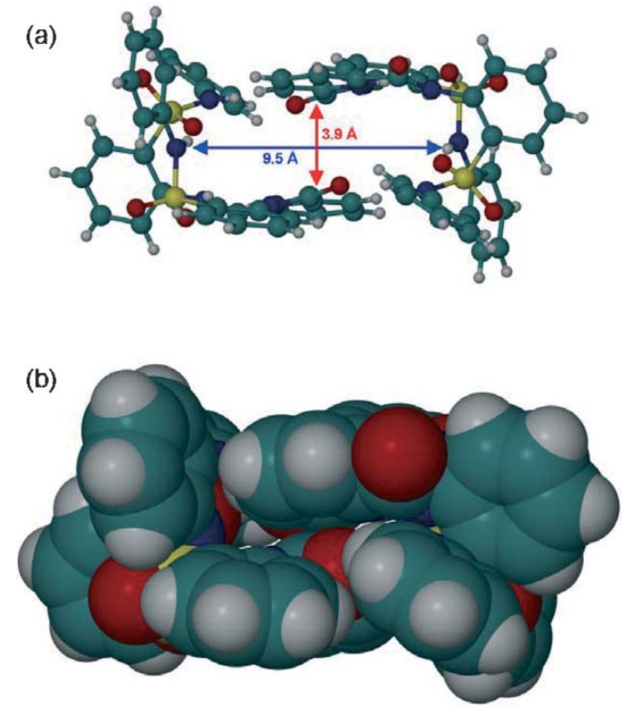

Fig. 1 Dimeric association of two L-shaped molecules in (a) ball-and-stick and (b) space filling representations.

crystallises as a low-density polymorph containing discrete lattice voids of approximately 235 Å^3 (depending on the method of calculation).[9] Close inspection of the structure reveals that it is not possible to map channels that interconnect these voids (Fig. 2). However, exposure of the crystals to liquid vinyl bromide for approximately fifteen minutes results in a single-crystal to single-crystal transformation during which vinyl bromide molecules become trapped in the lattice.[10] The single crystals survive the guest-inclusion process despite an approximately 6 Å shift of adjacent layers of host molecules relative to one another. Although the *material* is clearly permeable, it is not reasonable to suggest that the host *structure* remains substantially unaffected by guest uptake. Therefore this system does not conform entirely to the definition of crystal porosity as outlined above. A similar example was reported by Albrecht *et al.* who demonstrated the reversible uptake of gaseous SO_2 by an organoplatinum complex in a seemingly nonporous structure.[11] However, in the latter case the structural change experienced by the host lattice is far less dramatic than in the former: the relative positions of the host molecules do not change significantly, although coordination of SO_2 occurs with a concomitant (but slight) conformational change of the chelating ligand which constitutes part of the host molecule. In each of the above instances the crystal as a tangible material is shown to be permeable but, presented with at least two distinct structures, how do we decide which (if any) is the porous phase? Undoubtedly related examples are described in the literature and, taken together, serve to illustrate the point that claims of porosity are not always unequivocal, and that much depends on our own construal of the data.

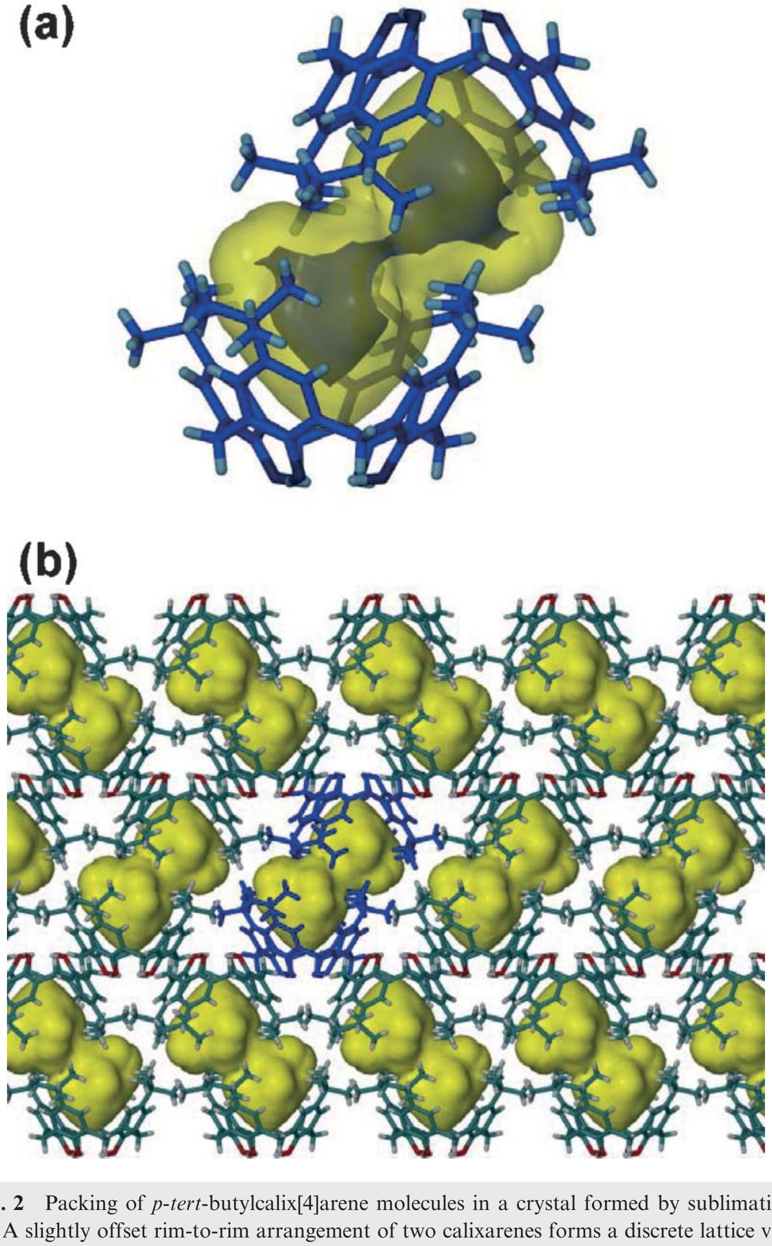

Fig. 2 Packing of *p-tert*-butylcalix[4]arene molecules in a crystal formed by sublimation. (a) A slightly offset rim-to-rim arrangement of two calixarenes forms a discrete lattice void of approximately 235 Å^3 as mapped by the contact surface (yellow, semi-transparent) of a probe with a radius of 1.5 Å. The dark inner surface represents the volume swept out by the centre of the probe and is termed the "accessible surface". (b) Two dimensional packing arrangement of calixarenes to form up–down bilayers. The voids are shown as yellow contact surfaces generated using a probe radius of 1.5 Å. The dimer shown in (a) is indicated in blue and it can be seen that the contact voids are not interconnected. Therefore, this structure is seemingly nonporous to a sphere of radius 1.5 Å.

When the guest-free crystals of *p-tert*-butylcalix[4]arene (described above) are exposed to air, carbon dioxide, methane and even hydrogen, the gases are absorbed to varying extents.[12] In these specific cases, X-ray studies show that the host lattice remains unaltered after guest uptake (*i.e.* atomic coordinates of the host molecules determined before and after guest uptake are the same within the tolerances permitted by their standard deviations). In a related study, a sublimed crystal of 5,11,17,23-tetra-*t*-butyl-25,26,27,28-tetramethoxy-2,8,14,20-tetrathiacalix[4]arene was shown to possess small lattice voids of 14, 16 and 36 Å^3, but no channels leading to these voids. After immersion in water for approximately 8 hours, X-ray analysis confirmed that water molecules had diffused through the seemingly nonporous and hydrophobic lattice to ultimately become embedded in the guest pockets.[13] To date the phenomenon of permeability in an apparently nonporous crystal has defied a simple explanation, but it seems likely that dynamic processes occur within the crystal during guest uptake whereby the host molecules cooperate with one another to create momentary windows of opportunity for guest diffusion to take place. However, it is difficult to determine the exact mechanisms of these processes experimentally owing to the ephemeral nature of the porosity.

Conventional porosity

Conventional porosity is easy to rationalise in terms of our understanding of molecular geometry. Zeolites fall into this category, as do many other systems based on either organic, inorganic or metal–organic compounds. One of the most common methods of obtaining conventionally porous crystals is to grow solvates with solvent molecules situated in channels defined by the host framework. Permeability is established if the solvent molecules can be removed completely, or exchanged for other guests without substantially disrupting the topology of the host framework. Furthermore, the size and shape of the channels can be used to rationalise the types of guest molecules that can potentially be included. However, it should be noted that volatile molecules are associated with kinetic diameters that do not necessarily comport with their van der Waals dimensions. For example, the kinetic diameter of hydrogen gas (2.89 Å) is larger than that of water (2.65 Å).

Are solvates porous?

In considering solvates, the relationship between porosity, permeability and host framework integrity is often complex. For example, it is well-known that desolvation of the vast majority of molecular crystals and even metal–organic frameworks almost always results in reorganization of the host to form a close-packed arrangement that scarcely retains any recognizable features of the original structure.[14] These solvent-removal processes seldom involve cooperativity between the host structural units (*i.e.* concerted motion that preserves the integrity of a single crystal). Thus the strain on the lattice caused by host rearrangement generally results in extensive fracturing of the formerly discrete crystal into a polycrystalline powder. In such cases permeability is certainly demonstrated by the loss of guest molecules by the *material*, but would it be appropriate to refer to such a system as being porous? If so, then the term loses its special significance and can be applied to any solvate. Presumably solvent loss occurs from a poorly understood intermediate phase consisting of an incommensurate (or non-cooperative[2]) collection of host molecules. It is usually not clear whether this process involves an intermediate short-lived porous phase, or whether the host molecules simply recrystallise without including guest molecules in their new apohost phase. Intermediate phases, and thus the exact mechanisms of desolvation, do not readily lend themselves to characterisation by diffraction techniques and to describe a poorly defined and transient phase as porous is thus unlikely to be meaningful.

Describing pores

In order to be of maximum use, any description of crystal porosity should be as comprehensive as possible. If known, the affinity for different kinds of guest molecules should be revealed. For example, would the host be more likely to include hydrophilic or hydrophobic guests? Are polarisable gases absorbed preferentially? Interrelated factors such as temperature, pressure, concentration, occupancy and uptake/release kinetics are highly relevant and should also be discussed. Most importantly, the size and shape of the pores should be described. To use a macroscopic analogy, the average door is porous to humans but perhaps not to an elephant. Thus use of the word "pore" to describe the door in this context should consider the nature of the guest. In general, a thorough description of a pore opening could conceivably involve a complicated topological treatment and thus pore metrics are often difficult to represent properly with a simple set of parameters. Usually it is more feasible to simply specify the maximum radius of a spherical probe that will pass through the narrowest region of a pore. This simplified approach is practicable in most cases since many channels are approximately circular in cross-section and volatile guests are usually associated with a kinetic diameter, implying that they can generally be approximated as spherical entities. Square or rectangular channels are also easily described using one or two parameters, respectively.

Mapping pores and cavities

One of the most important parameters associated with porous crystals is the amount of free volume within the material. Several computer programs are available for calculating solvent-contact (*e.g.* MSROLL[15]) or solvent-accessible volumes (*e.g.* PLATON[16]) which are normally represented as their bounding surfaces (see Fig. 2a). These routines map the volume that a spherical probe of given radius can sweep out within a molecular void or channel and the results of these calculations tend to be highly sensitive to the probe radius chosen, as illustrated in Table 1. It is therefore imperative to use a sensible probe radius in order to realistically represent the space available to a particular guest. A smaller probe radius results in a larger estimated free volume, but choosing a probe radius smaller than that of a hydrogen atom (1.17 Å) is clearly meaningless (typically, probe radii of 1.4 to 1.7 Å produce meaningful results). Furthermore, the probe radius can dramatically influence whether or not a structure should be considered to be conventionally porous, as illustrated by the packing in sublimed (*i.e.* guest-free) crystals of Dianin's compound (Fig. 3). The crystal packing mode of the racemic mixture of Dianin's compound is well-known in the field of solid-state supramolecular chemistry. Six molecules aggregate to form a hexagonal hydrogen bonded arrangement of hydroxyl moieties. The *R* and *S* enantiomers alternate about this ring with three *R* enantiomers projecting above the plane of the

Table 1 Calculated[15,18] cavity volumes (*i.e.* bounded by contact surfaces) for dimeric *p-tert*-butylcalix[4]arene shown in Fig. 1a

Probe radius (Å)	Cavity volume (Å^3)
1.3	270
1.4	254
1.5	237
1.6	226[a]
1.7	212[a]

[a] Probes with radii ⩾ 1.6 Å are unable to traverse the constriction at the centroid of the dimer and therefore two cavities of identical size and shape are obtained. In these instances, the combined volume of the two cavities is given.

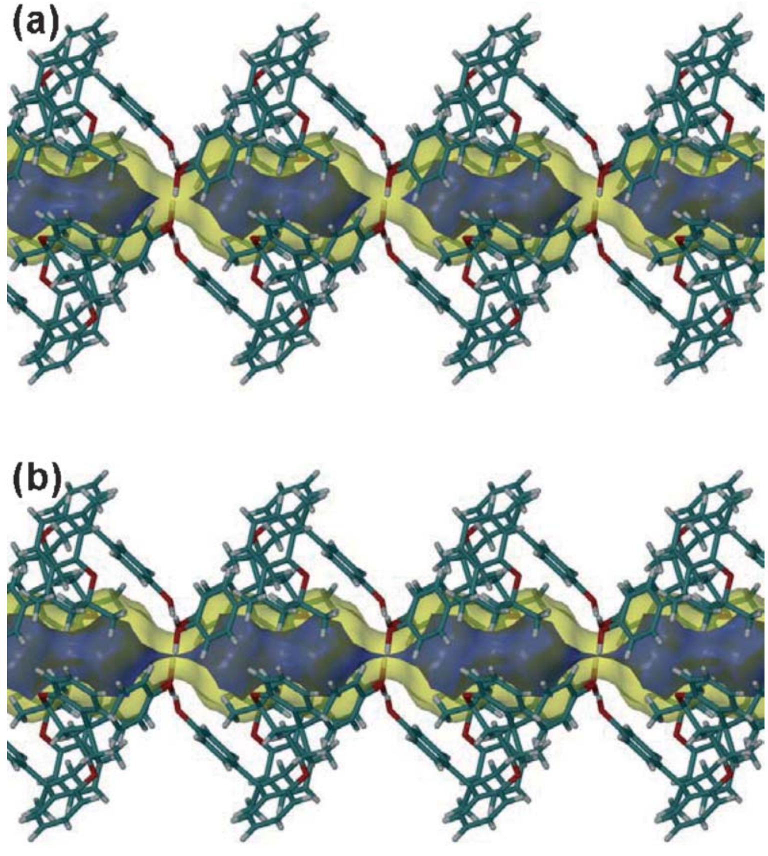

Fig. 3 Dianin's compound forms linear columns of hexamers that enclose cavities. Depending on the probe radius, and considering the structure to be static, the cavities are either isolated from one another, or interconnected *via* an aperture formed by a cyclic arrangement of six O–H···O hydrogen bonds. (a) Using a probe radius of 1.3 Å, the contact surfaces (yellow, semi-transparent) represent an infinite channel although the probe sphere cannot pass from one cavity to the next as shown by its accessible surface (blue). (b) A probe of radius 1.2 Å forms a contact surface similar to that shown in (a). However, the accessible surface is continuous, implying that the 1.2 Å probe can just pass through the hexameric hydroxyl aperture from one void to the next. Thus Dianin's compound is porous to a probe of radius 1.2 Å but not to a probe of radius 1.3 Å.

hexagon and three *S* enantiomers below the plane, thus approximating two divergent cups. Adjacent hexamers are stacked in an infinite column perpendicular to the hydrogen bonded ring such that their cups interdigitate by means of van der Waals interactions to form an infinite columnar series of cavities. While a probe of radius 1.3 Å is too large to pass from one cavity to the next through the hydrogen bonded ring, a probe of radius 1.2 Å is able to pass through. Therefore, by considering the static atomic coordinates of the host framework of Dianin's compound, the crystals are conventionally porous to a probe of radius 1.2 Å, but not to a probe of radius 1.3 Å. The purpose of this example is to illustrate that, when describing a structure as being conventionally porous, it is imperative to specify the probe radius. Fig. 3 also shows that a continuous *contact* surface does not imply porosity since it is possible for contact surfaces of adjacent cavities to merge without allowing the probe to pass from one cavity to the next. Indeed, the true test of conventional porosity in such cases is whether or not the *accessible* surface is continuous.

Summary

The study of porosity in the context of crystal engineering is rapidly growing in intensity. In a recent tutorial review discussing the evolution of porous frameworks, Kitagawa[17] outlined much of what has been described in this contribution and specifically mentions that use of the term "porous" requires that porosity be verified by gas sorption experiments. These views are not new to the community of researchers concerned with studies of porosity. My own position is that true porosity in crystals is still a relatively rare and and a very special phenomenon and it would be regrettable if indiscriminate use of the term ultimately diminishes its impact.

Acknowledgements

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