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Don't be Square: Why do Chemistry and Nature Build Hexagons?^a

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Abstract: This article distinguishes the role of hexagonal motifs in close-packed solid-state structures and in graphite and graphene; we then illustrate how hexagonal cells in the nests of honey bees and paper wasps minimize construction materials while optimizing space and achieving a robust architecture from delicate materials.

Keywords: Chemical education · Close-packing · Graphite · Hexagonal motif · Honey bee · Paper wasp

Early in most chemistry courses, students encounter the concepts of close packing of spheres as a model for the arrangement of atoms in metallic solids. The model assumes that atoms are hard spheres but, of course, this is not consistent with modern theory. Nonetheless, it is a valuable teaching tool provided that students are reminded that treatments of the solid state using hard spheres are only approximate models. The prototypes for close packing are hexagonal close packing (hcp) and cubic close packing (ccp), also known as face-centred cubic (fcc). Single layers in either of the hcp or ccp structures are identical and contain a hexagonal motif of six spheres packed around a central sphere. Fig. 1a illustrates two adjacent layers in an hcp arrangement of spheres; the packing continues in an ABAB... sequence. In a ccp arrangement, the sequence of layers is ABCABC... (Fig. 1b). Close packing optimizes the packing efficiency, and in both hcp and ccp, 74% of the available space is occupied by spheres. Other packing arrangements have lower packing efficiencies, for example, 68% and 52%, respectively, in body-centred cubic and simple cubic arrangements.^[1] Each atom in a close-packed array has 12 near neighbours: six in a given layer and three in each of the layers above and below.

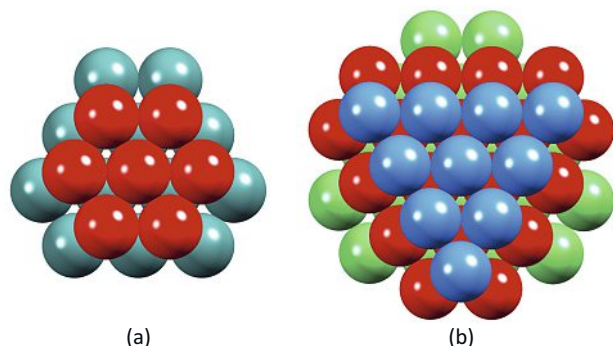


Fig. 1. Close packing of spheres: (a) hexagonal close packing with a sequence of layers ABAB.... and (b) cubic close packing with a layer sequence ABCABC.

Another well-known example of a hexagonal motif in chemistry is the structure of graphene (Fig. 2a) which comprises a single sheet from the structure of graphite (Fig. 2b). The bonding in graphene and graphite is described by sp^2 hybridized C atoms, each forming three C–C σ -bonds. One valence electron per C atom is part of a delocalized π -system which gives rise to electrical conductivity in a direction through the plane of the sheet. In α -graphite, the electrical resistivity (the resistance to an electrical current and the inverse of electrical conductivity) is $1.3 \times 10^{-5} \Omega \text{ m}$ at 293 K in a direction parallel to a plane; in contrast, it is *ca.* $1 \Omega \text{ m}$ in a direction orthogonal to the planes. In graphene, the electrical resistivity in the plane of the sheet is even lower (of the order of 10^{-6} to $10^{-8} \Omega \text{ m}$ at room temperature).

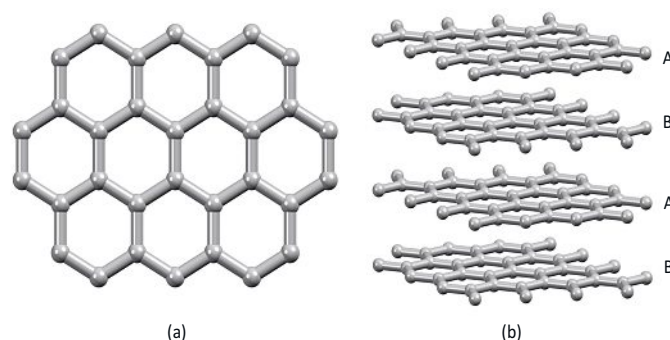
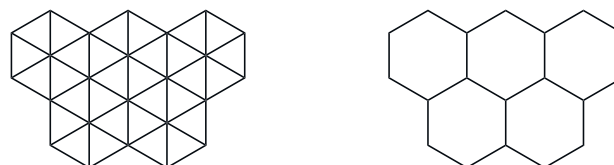


Fig. 2. (a) Part of the structure of graphene, and (b) the stacking of sheets is an ABAB... arrangement in α -graphite. As an aside, the structure of graphite was first determined by powder X-ray diffraction in 1916 by Peter Debye and Swiss physicist Paul Scherrer,^[2] after whom the Paul Scherrer Institute is named.

Notice the significant difference between Figs. 1 and 2a. Close-packing of spheres is actually built upon triangular domains whereas the 3-connecting carbon atoms direct a hexagonal net or honeycomb structure as shown below:



The description *honeycomb* gives us the link to Nature and to social honey bees in the family *Apis*. Honey bees (both wild and domestic) construct combs from beeswax, and Fig. 3a illustrates the characteristic hexagonal array of cells which make up the comb. Each cell either stores food (pollen or honey) or contains the eggs, larvae and pupae of the developing stages of the bees. Bees collect both pollen and nectar from flowers. The long pro-

boscis (Fig. 3b) is used to reach nectar which is transferred into one of the bee's two stomachs. In one stomach (the so-called honey stomach), the enzyme invertase acts on the nectar breaking down polysaccharides to monosaccharides including glucose and fructose. Once the bee returns to the beehive, the contents of the honey stomach are expelled through the proboscis into empty cells in the honeycomb. Nectar contains, on average, 70–80% water, and the social bees work together to reduce the water content of the nectar by using their wings to fan the comb, thereby raising the temperature and evaporating water to reach a water content <20%. The combination of enzyme action and removal of water converts nectar to honey. Pollen is also stored in the comb and being a vital source of protein, is mixed with honey (carbohydrate) as larval food.



Fig. 3. (a) Honeycomb of domestic Western honeybees showing pollen and honey stores. The honey cells are capped (pale yellow) and the pollen stores are uncapped; bees use the fresh pollen rapidly because, unlike honey, the storage lifetime of pollen is short. The rectangular shape of the comb is constrained by an artificial wooden frame. (b) Western honeybee (*Apis mellifera*) showing the long proboscis. Credits: (a) Paul Booth; (b) Edwin Constable.

But why are the cells in the honeycomb hexagonal? Why not square or circular? The earliest postulate can be found in the three books on agriculture by the Roman Marcus Terentius Varro who wrote in ca. 37 BCE (translated in 1918)^[3]: “Has not each cell in a honeycomb six sides, or as many as a bee has feet, the art of which arrangement appears in the teaching of the geometers that of all polygons the hexagon covers the largest area within a circle.” The question remained a conundrum. In 1859, Charles Darwin^[4] wrote: “We hear from mathematicians that bees have practically solved a recondite problem, and have made their cells of the proper shape to hold the greatest possible amount of honey, with the least possible consumption of precious wax in their construction.” In 2001, Thomas Hales published a mathematical proof that hexagons organized in a grid minimize the total perimeter of any subdivision of a plane into regions of equal area,^[5] i.e. hexagons are more economical than other possible shapes such as squares or circles. If we take into consideration that the biosynthesis of beeswax from honey by bees is a costly process in terms of energy,^[6] then we see consistency between Hales’ proof and Darwin’s statement. A point of note is that the first person to experimentally demonstrate that bees synthesize wax from honey was the Swiss naturalist François Huber (1750–1831).

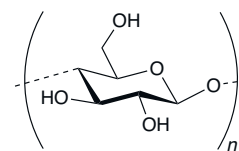
The construction and material properties of honeycombs shed further light on Nature’s engineering of the hexagonal cell-containing architecture. A pristine honeycomb is extremely lightweight, but when laden with pollen, honey, nectar, bees and their larvae, the weight can increase to several kilograms.^[7] Beeswax is a complex mixture of organic compounds including hydrocarbons, mono-, di- and triesters, carboxylic acids and alcohols. It is a rather delicate material, but using time-resolved X-ray micros-

copy, Chawla and coworkers have been able to establish how a robust assembly results. Initially, the bees deposit wax to produce a ‘corrugated spine’ and the latter is the substrate for the growth of all hexagonal cells. The video available in the supplementary material for Chawla’s open access publication^[7] illustrates the emergence of the hexagonal symmetry.



Fig. 4. Nests of paper wasps in the subfamily *Polistinae*. Credit: Edwin Constable

Bees are not alone in constructing nests containing hexagonal chambers. Wasps in the family *Vespidae* include social paper wasps in several subfamilies including *Polistinae*. The latter construct nests exemplified by those in Fig. 4. However, unlike a construction material of wax, paper wasps use wood or other plant pulp (i.e. cellulose, Scheme 1) combined with saliva. This requires energy-consuming effort in collecting wood (by chewing) and water. As for bees, the design of the nest of a paper wasp has evolved to minimize the use of building materials while optimizing space for accommodating eggs and larvae and providing a robust architecture from a fragile material. An interesting difference between the nests of honey bees and paper wasps is that bees construct a double-sided comb, whereas a single-sided comb is typical of paper wasps. Fig. 5a shows the pristine comb of wild bees *Apis mellifera* when unconstrained by artificial frames. The end of each hexagonal cell terminates in a structure consisting of three rhombuses (Fig. 5b). Pairs of honeycombs fit exactly together back-to-back as can be appreciated by inspection of Fig. 5.



Scheme 1. Cellulose is a polysaccharide comprising β -D-glucose repeat units.

Biomaterials such as those found in the bee and wasp combs described above, are the inspiration for many artificial materials. Two up-to-date reviews provide a wide coverage of honeycomb-inspired materials including design strategies, fabrication processes and applications.^[8,9]

In this article, we have highlighted the role of hexagonal motifs in close-packed solid-state structures and in graphite and graphene. This led to a discussion of why social honey bees and paper wasps construct their nests (combs) with hexagonal cells: it minimizes construction materials while optimizing space and achieving a robust architecture from delicate materials.

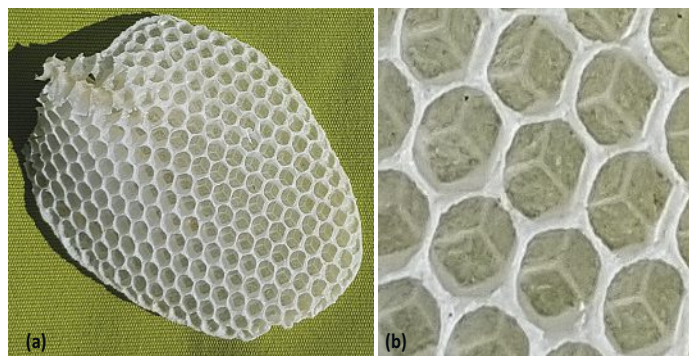


Fig. 5. (a) Wild comb of honey bees *Apis mellifera*, and (b) enlargement of the cells to show the pyramidal structure that closes the cell and the complementary honeycomb that fits back-to-back with the layer facing the reader. Credit: Paul Booth.

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*This column is one of a series designed to attract teachers to topics that link chemistry to Nature and stimulate students by seeing real-life applications of the subject.