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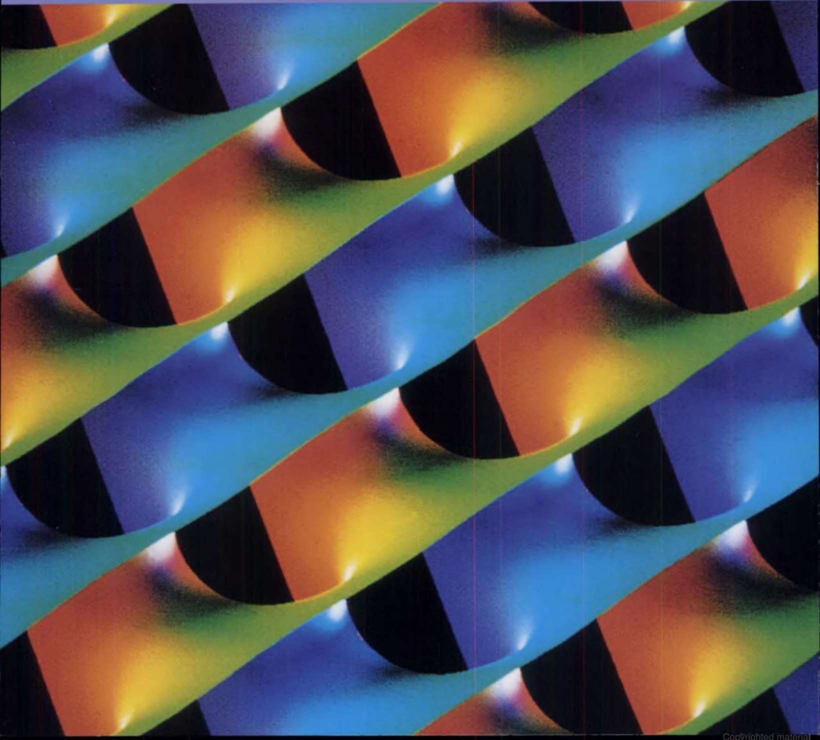
Designing the Molecular World

Chemistry at the Frontier

Philip Ball



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Philip Ball
London, September 1993

Designing the Molecular World

Introduction

Engineering the Elements

He who understands nothing but chemistry doesn't even understand chemistry.

Georg Christoph Lichtenberg

How to Avoid Science

A good way in a science lesson is to wait until some old fashioned poison like sulphurick acid etc. turns up. As per ushual science master, who not forward-looking, sa: No boy is to touch the contents of the tube.

Make up tube which look the same and place alongside acid. Master begins lesson drone drone drone. Sudenly you spring to feet with grate cry: 'Sir Sir I can't stand it any longer!'

Drink coloured water and collapse to be carried out as if dead. n.b. if you make a mistake with this one you are still carried out as if dead and you *are*.

Geoffrey Willans and Ronald Searle
Down With Skool!

Even that most aberrant of schoolboys Nigel Molesworth would have to admit that there are times when it pays to have a little knowledge of chemistry. It remains, however, one of the least glamorous of sciences. Physicists, by comparison, are to be found pondering the deepest mysteries of the Universe: Where did everything come from? What will happen to it all? What is matter? What is time? Physics represents science at its most abstract, and also on its grandest scale, as gigantic telescopes search the heavens for the echoes of creation and particle accelerators miles in diameter smash subatomic particles into each other in order to glean clues about what the world is made of. The questions tackled by biologists, meanwhile, are the matters of life and death – it is for them to take up arms against the thousand natural diseases that flesh is heir to, or to strive towards understanding how we evolved from sea-bound blobs of jelly. Geologists brave the awesome fury of volcanoes and earthquakes; oceanographers plumb the hidden depths of the world. What do chemists do? Well, they make paint, among other things.

One might expect to find nothing more of interest in the practice of making paint than in watching it dry. But there is, as I hope to convince you later, a subtlety and cleverness to the art. If that still seems a prospect wanting in enticement, let me mention that we will also see what paint has in common with living cells and soap bubbles, with muscle tissues and plastics. The tiny corner of chemistry in which paint is contrived holds unguessed surprises, and supplies as good an illustration as any other of the way in which an understanding of the chemical nature of substances helps us to control the shape and form of our world. For the truth is that, while many of the other sciences are associated with mysteries of an awe-inspiring scale, chemistry is the science of everyday experience, of how plants grow and how snowflakes form and how a flame burns.

Yet chemistry has acquired the image of a mundane pursuit; and it must be said that some blame resides with chemists themselves, many of whom seem resigned to accept a perception of their research as worthy but dull. It is true that chemists are hampered from the outset by low expectations. (According to the fossilized wit of Oxford, the chemist (invariably male) is a dour clod with long hair and dirty hands – a formidable beer-swigger perhaps, but a social gorilla.) Yet chemists themselves often insist on a humility that borders on insecurity. They will say at conferences, "I don't claim to understand these results – I leave that to the physicists. All I did was make the materials."

I have no crusade in mind, however. Rather, what this book aims to do is to present a selection of some of the things that a chemist today may find her- or himself engaged in studying. If by doing so it succeeds in demonstrating simply that the new chemistry is no longer a matter of test tubes and bad smells (although both may be encountered along the way), that is fine enough. For this demonstration we will need to take a cursory glance not only at some of the basic principles of chemistry but also at a pot-pourri of ideas from disciplines as diverse as genetics, climatology, electronics and the study of chaos. Yet this is most certainly not a textbook: it will not cover chemistry comprehensively, nor will it provide a rigorous scientific description of the phenomena that will be discussed. Simply, I hope to show that in order to discover a sense of wonder about the world, it is not always necessary to look to the stars or to the theory of evolution; one can look instead at the washing-up liquid, the leaves on a tree or the catalytic convertors in our cars.

In 1950 the distinguished American chemist Linus Pauling said "Chemistry is a young science." It is true that chemistry of a sort was practised in Ancient China, in

Babylonia and beyond, but you could see his point. At that time only a few decades had passed since we had come to understand the constitution of the atom, chemistry's building block; and Dmitri Mendeleev's Periodic Table of chemical elements was just 81 years old, with several of the gaps only recently filled. But almost half a century later, does chemistry still retain any of its youthful vigor?

Much of chemistry today is becoming motivated and guided by principles dramatically different from those that informed Pauling's comment. The new chemistry pays scant regard to the disciplines into which the topic has been traditionally divided. At college, chemistry still is often taught in three distinct chunks: physical, organic and inorganic. But few are the chemists today who claim firm allegiance to a single one of these branches; rather, novel concepts and classifications are emerging through which researchers define their work. I shall give here an incomplete list of some of these; we will find these ideas cropping up many times in the subsequent chapters, often lending a common thread to studies that otherwise appear disparate. If you can, bear them in mind in what follows.

Materials: There may be many who lament the dawn of the plastic age. It has, however, demonstrated in unambiguous terms that we are no longer forced to manage as best we can with the materials that the natural world provides – we can design new ones that better suit our purposes. Plastics now have a seemingly limitless variety of properties: they show tensile strengths comparable to steel, they can dissolve in water or be eaten by microbes, conduct electricity, change color or contract and flex like muscles. Plastics generally consist of carbon-based chain-like "polymer" molecules; polymers based on silicon and oxygen, meanwhile, serve as the precursors to new kinds of ceramic materials, "artificial rocks" that promise new limits to hardness and strength.

The explosion of interest in materials science in recent years has gained tremendously from the realization that an understanding of the structure of materials at the molecular level can lead to the design of properties useful at the engineering level. We can now control the growth of materials atom by atom, opening up new possibilities in semiconductor microelectronics for example, or allowing the possibility of mimicking the impressive design of natural substances like bone and shell. And as our ability to control the microscopic structure of materials improves, chemistry continues occasionally to produce materials with unforeseen surprises in store, such as the carbon cages known as fullerenes or the metal alloys called quasicrystals.

Electronics: Did I say plastics that conduct electricity? Yes, not only do they exist but they are already being used in electronic devices. A broad range of synthetic chemical compounds are now known that possess metal-like electrical conductivities, and some even show the remarkable property of superconductivity – conductivity without resistance. Magnets too can now be made without a metal in sight, based on carbon- and nitrogen-containing molecules more like those found in the organic world. An entire electronics industry is beginning to look feasible that has no need for metals or conventional semiconductors such as silicon. For some, the ultimate dream is to build circuits from individual molecules, using conducting molecular wires to link up atomic-scale components into incredibly compact "molecular devices."

While one approach to molecular electronics is to make conventional microelectronic devices from unconventional materials, a still more daring suggestion is to set aside the familiar diodes and transistors and look for inspiration from nature. Photosynthesis, for instance, involves the passing from molecule to molecule of tiny electric currents within the cells of living organisms, while other biomolecules regulate currents as if they were themselves miniature electronic devices. Gaining an understanding of how these natural devices work will open doors to a kind of "organic" electronics.

Self-assembly: If, as hinted above, we want to build molecular structures one molecule at a time, we will need much more precision and speed at manipulation than is available to today's engineers of the microworld. But there is an alternative to the laborious process of molecule-by-molecule construction: get the molecules to assemble themselves. This might seem like expecting a house to suddenly leap together from a pile of bricks, but molecules are much more versatile than bricks. Soap molecules, for instance, can aggregate spontaneously into all manner of complex structures, including sheets, layered stacks and artificial cell-like membranes. Other organic molecules show the ability to organize themselves into the variety of orderly arrays that we recognize as liquid crystals.

The better we understand the way that molecules interact, the more able we will be to design them so that they assemble themselves into these intricate structures. Here again there is much to be learned from nature, which abounds with molecules that can recognize and team up with others in very specific and organized ways. Both in nature and in the laboratory, molecular "recognition" and self-assembly can lead to the possibility of molecules that put together copies of themselves from their component parts, or in other words to . . .

Replication: One of the primary attributes of a living organism is that it be able to make replicas of itself. There is nothing about this ability that requires a motivating intelligence, however; chemistry alone can do the job. The discovery, in 1953, of the structure of DNA led the way to an understanding of how chemical replication is possible. The replicating molecule acts as a template on which a copy is assembled; and this assembly process involves "complementarity" – a pairing up of structural elements – so that the molecule provides a scaffolding for construction of its replica.

It is now clear that molecules don't have to be anywhere near as complex as DNA in order to be able to replicate – small molecules and molecular assemblies have been devised that can do this in a test tube. In some sense, these molecules represent the first step towards a kind of artificial life. But as the raw materials provided to these synthetic replicators are generally not far removed from the end product, they are not so much building copies from scratch as simply speeding up the rate at which the final stages of replication take place: genuine synthetic life is still a long way off. However, the discovery in 1982 that DNA's relative RNA can perform the trick of replication all by itself (that is, without an army of helper molecules such as DNA requires) may provide a vital clue to our understanding of how life evolved through chemistry alone.

Specificity: Chemical reactions can be notoriously messy affairs, leaving one with the unwelcome task of extracting one's intended product from a whole host of substances produced in side reactions. That this simply does not happen in the biochemistry of the body, where each reaction generally gives just the one desired product, suggests that we need not resign ourselves to such a state of affairs in our own clumsy attempts at chemical synthesis. And indeed, by exploiting the principles of molecular recognition found in biology, these efforts are becoming progressively less maladroit. We are learning how to make chemistry specific.

It is the class of molecules called enzymes that is responsible for the remarkable specificity of biochemical processes. Despite a still far from complete understanding of how enzymes function, synthetic molecules have been designed that can mimic many of their attributes. The chemical industry, meanwhile, is learning how to exploit the exquisite chemical control that enzymes display by setting them to work in "bioreactors," biologically based chemical plants which produce complex pharmaceutical products that are otherwise beyond our wit to synthesize. And petrochemical companies are finding that the minerals known as zeolites can function as rudimentary "solid-state enzymes" to provide useful compounds from crude oil.

Seeing at the atomic scale: The process of chemical change happens in the twinkling of an eye. During the course of a chemical reaction, the interaction of two molecules may occupy no more than a trillionth of a second. In the past this has posed tremendous difficulties for attempts to discover exactly what goes on when molecules get together, but there now exist ways to capture these incredibly brief events "on film." Lasers that pump out thousands of discrete light pulses during the time it takes for individual molecules to interact allow one to capture snapshots of molecular motions frozen in time. We can now watch molecules as they tumble, collide and become transformed into new arrangements of atoms.

Microscopes, meanwhile, are letting us see matter at the scale of individual atoms. These abandon the use of light and employ electrons instead to obtain images of objects so small that many millions would fit on a pinhead. The regularly packed lattice of atoms in a crystal, the orderly stacks of molecules in a liquid crystal film or the double helix of DNA – all have been revealed by this new brand of microscope.

Nonequilibrium: The many complex shapes found in the natural world, ranging from snowflakes to the roots and fronds of plants, have long represented a source of fascination and bafflement alike to natural scientists. But one of the astonishing discoveries of recent years is that complicated patterns do not necessarily require a highly controlled process of formation; rather, they can arise spontaneously in systems that appear to be wildly out of control. Systems that are far from attaining any sort of equilibrium need not descend into disorder but may, under appropriate conditions, organize themselves into large-scale patterns that may be at once very intricate and beautifully symmetric. The "forbidden crystals" known as quasicrystals provide one such example; others display so-called "fractal" properties, appearing identical regardless of how closely one looks at them.

Systems far from equilibrium frequently exhibit dynamic, moving patterns which persist even though the system is constantly changing. Nonequilibrium chemical reactions produce propagating chemical waves, like spiralling whirlpools or ripples radiating from a splash in a pond. Oscillating, periodic behavior in nonequilibrium systems is a common precursor to the onset of complete unpredictability – that is, to chaos. The hallmarks of chaos have now been identified in several chemical reactions.

Mesoscale chemistry: Our understanding of chemical processes is now fairly well advanced at both the macroscopic scale – that at which we can see and touch – and the microscopic or molecular scale. But the region in between – the mesoscopic scale, by which typically we mean sizes ranging from thousands of atoms to those of living cells – contains much uncharted territory. Will assemblies of a thousand or so molecules behave like a lump of bulk material or still much like individual molecules? The answer often turns out to be neither: entirely new properties may be observed at these scales.

Our new-found ability to induce self-assembly of molecules into large structures such as artificial membranes or ordered liquid crystalline arrays has opened up this middle ground for investigation. We can also condense atoms from a vapor into clusters of any desired size, from just three or four atoms to many thousands, and thereby follow the way that properties change as the system develops from a molecular object into a piece of bulk solid. This evolution sometimes gets stuck at anomalously stable "magic numbers" of atoms, the reasons for which are still incompletely understood. One example of particular interest is provided by clusters of carbon atoms, which have the ability to arrange themselves into hollow cages of very specific sizes. These carbon cages are providing entirely new directions for research in chemistry, electronics and materials science.

Energy conversion: Many chemical reactions produce energy, usually in the form of heat. We have been able to exploit this fact to our benefit ever since mankind tamed fire; but it is not a little remarkable that our principal means of energy generation today continues to involve a chemical process as crude and inefficient as combustion. The more direct conversion of chemical energy into electrical energy is carried out by batteries, but these are not cheap or powerful enough to meet a significant part of the world's demand for power. Nevertheless, new kinds of battery are now being developed that promise to bring novel applications: as power sources in cars or on space satellites, for instance. Extremely small, compact and lightweight batteries provide efficient, safe and convenient energy supplies in all manner of situations that do not require vast output power.

We receive millions of megawatts of energy for free every day by courtesy of the Sun, but have few efficient means of capturing this energy and converting it to more useful forms. Solar cells are chemistry's answer: they employ materials that absorb light and store it away in the form of chemical energy or channel it directly into electricity. Modern solar cells are now taking cues from nature's own version, the photosynthetic reaction centers in plants.

Sensors: The ability to detect, quickly and efficiently, the presence or absence of specific chemicals can be a matter of life or death. Leaks of toxic gases, monitoring of glucose or of anesthetics in the bloodstream, testing for harmful compounds in foods – all require reliable and sensitive sensing devices. Many chemical sensors rely on electrochemical principles, whereby the relevant chemical species induces a change in electrical current or voltage at an electrode. Sensors of this kind which display a highly specific response to certain biochemicals are today being developed by exploiting the molecular recognition capabilities of natural enzymes. Polymer science, meanwhile, is able to supply plastic membranes which can be made selectively permeable to one kind of molecule but impenetrable to others.

In some specialized situations, the ultimate in detection sensitivity – detecting single molecules – is now possible. This outperforms even the capabilities of our own primary chemical sensor, the nose's olfactory system. Sensing via spectroscopy – the interaction of molecules with light – conveys the advantage that the substances do not have to encounter the sensing device physically, but rather can be very distant. In this way, chemical compounds can be monitored in the remote atmosphere or in interstellar space and the atmospheres of stars.

The environment: Humans have been discharging chemical wastes into the rivers, oceans, soil and air for as long as we have been on the planet. But now that the consequences of these actions are finally coming home to roost, we are being forced to take an unprecedented interest in the chemical composition of our environment. Pollution from Europe shows up in Arctic snow; flue gases from power-generating plants fall back to the ground in the form of acidic rain; gases previously thought too inert to pose a hazard are now causing erosion of the ozone layer. And the product of combusted carbon compounds, carbon dioxide, threatens to turn the planet into a sweltering greenhouse.

The chemical processes responsible for these environmental hazards are now becoming well understood, but their effects on the planet's ecology and climate are harder to predict. There are clues to be had, however, from studying the way in which changes in the atmosphere's chemistry, induced by purely natural processes, have warmed or cooled the planet in the past. Scientists are studying the composition of ancient air trapped in ice bubbles, and of sedimentary rocks deposited long ago on the ocean floor, in attempts to understand the links between atmospheric chemistry and climate change.

Others, meanwhile, trace out the paths by which metals are cycled in the atmosphere and oceans to gain insights into the transport of pollutants. And researchers are laboring to find safer replacements for the substances that are endangering or littering the planet:

alternatives to ozone-destroying CFCs, for instance, or plastics that can be broken down by bacteria.

I have divided this book into three parts. The first four chapters are concerned with some of the traditional aspects of chemical research – structure and bonding, thermodynamics and kinetics, spectroscopy and crystallography (Chapters 1 to 4, respectively). They will illustrate, I hope, that this tradition is a changing one, whereby established tools and concepts are being adapted to meet new aims and challenges. Some themes in science become obsolete and fall by the wayside once they have served their purpose, but in these four areas, at least, new discoveries and technological advances have guaranteed a valuable role for "traditional" approaches for decades to come.

Of the three chapters that follow in Part II, only the theme of Chapter 7 (colloid chemistry) might have meant anything to researchers of the 1950s, and even then its relevance would have borne little similarity to that of today. We will see in these chapters how advances in understanding at the molecular level are leading to entirely new ways of looking at chemical properties and reactions and are helping to bridge the divide between chemistry and disciplines such as molecular biology, electronics and materials science. In short, we will look at some of the new *functions* of chemical research.

In the final part I will discuss some aspects of what I call "chemistry as a process." That is to say, I will be less concerned with chemical change in terms of the products and mechanics of chemical reactions and interactions, and more with the consequences of these processes at a higher level. Life itself is one such consequence, having arisen from chemistry on the early Earth (Chapter 8); complexity of growth and form in the natural world must also evolve somehow from simple chemical processes (Chapter 9); and many of the important changes in our atmosphere, environment and climate (Chapter 10) have their origin in chemical transformations.

In the course of talking about these matters, I have exhausted the space that some chemists might wish to have seen devoted to other topics. Most notably, it is hard to find an excuse for saying relatively little about polymer science and electrochemistry. I can but ask for forbearance here; in the bibliography, however, you will find a few pointers to sources that might serve to plug these holes.

Part I

The Changing Tradition

1

How It All Fits Together

The architecture of molecules

> *The domain in which chemical synthesis exercises its creative power is vaster than that of nature herself.*
>
> Marcellin Berthelot

In 1989, chemists working at Harvard University in Massachusetts brewed up a horribly lethal concoction called palytoxin – one of the most poisonous natural chemicals known and the most toxic ever to be synthesized artificially. No sinister motives lie behind this accomplishment, however. The Harvard chemists set their sights on palytoxin simply because building it "from scratch" represented such an extraordinary challenge.

A glance at Figure 1.1 might persuade you of the enormity of the task. This illustration shows the structure of the palytoxin molecule – the balls represent atoms, while the sticks linking them represent chemical bonds. (If you find the concepts of an atom, a molecule and a chemical bond unfamiliar or vague, don't despair; all will be explained shortly. But even without this understanding, you can appreciate that putting together such a complex object is no mean undertaking.) There is no important use for palytoxin. Its synthesis was a little like those recitals from memory of the Holy Bible or of the number pi to a million decimal places: a pure demonstration of technical prowess. Yet by tackling difficult tasks such as this, chemists are likely to discover new ways to solve problems that crop up in the synthesis of the complicated molecules needed by industries and by medical science.

Building molecules is big business, and understandably so. For although nature has provided us with a tremendous selection of substances with which to construct

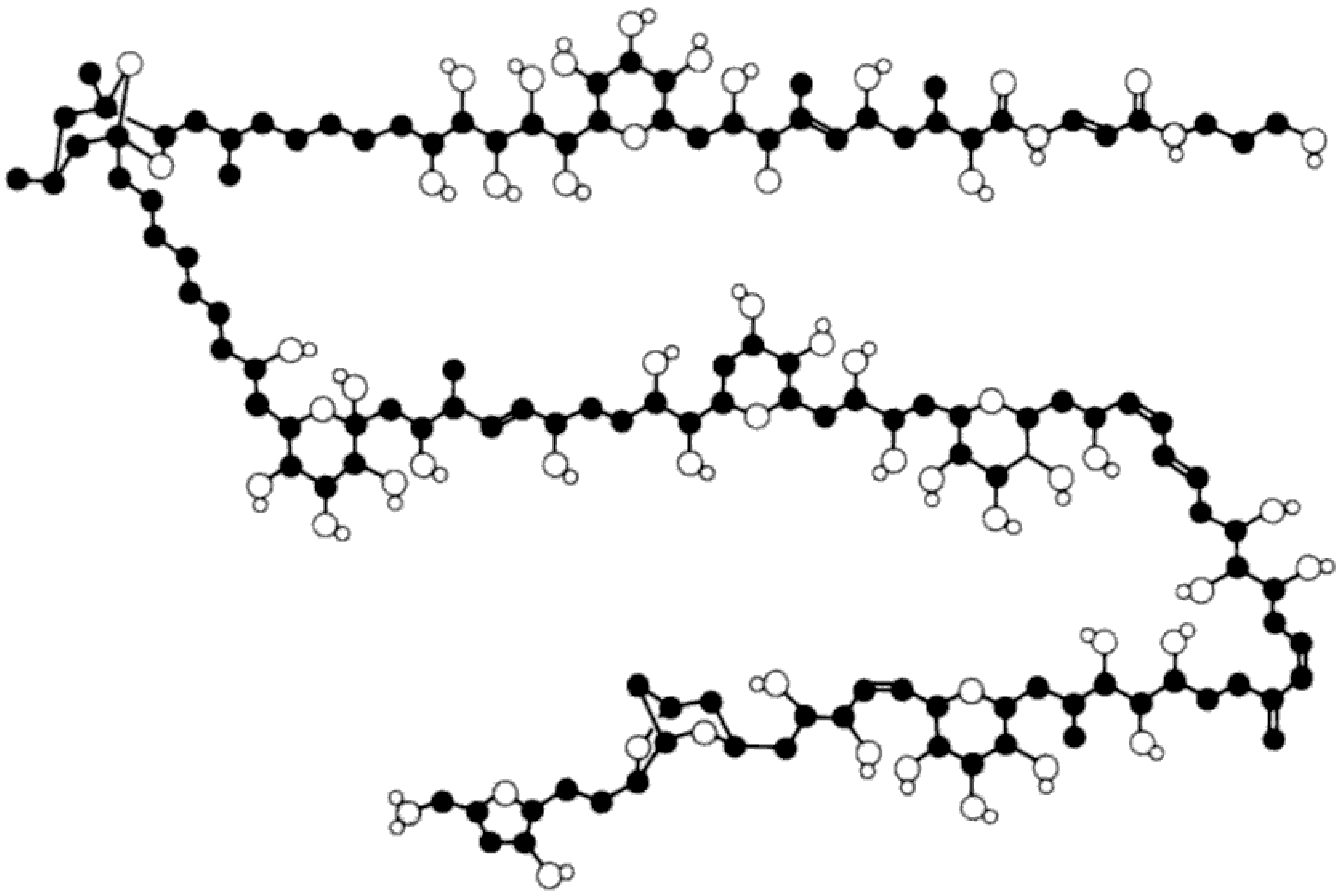


Figure 1.1 *The molecular structure of palytoxin, simultaneously one of the most complicated and the most toxic compounds ever synthesized. The black circles represent carbon atoms, the large white circles oxygen, the gray circles nitrogen and the small white circles hydrogen. For clarity, hydrogen atoms attached to carbon are not shown.*

civilizations and improve the lives of its citizens, their range and abundance appears insufficient to meet our every need. The great variety of complex substances found in the living world, particularly in plants, has proved to be immensely valuable to physicians throughout the ages, but there are ailments for which natural cures are rare, ineffective or nonexistent. A great many chemists are therefore engaged in the enterprise of creating purely artificial substances that provide cheaper or more potent alternatives, or which can fill the gaps. The pharmaceutical industry is just one of the spheres in which artificial or synthetic substances are called for, but it is probably the example *par excellence* because the substances that it requires are often extremely sophisticated and accordingly hard to make.

In later chapters we will encounter some of the simpler synthetic molecules created via the techniques of modern chemistry. In general these are constructed from smaller molecules which are joined together or rearranged in chemical reactions. I don't propose to look at these techniques of synthesis in any detail – they are often ingenious, but in all honesty they don't hold much intrinsic interest for the nonchemist. There is more fun to be had, I feel, from looking at the behavior and the properties of the molecules that come out in the end. In this chapter, nevertheless, I do intend to take a close look at the synthesis of one particular molecule, which rejoices in the baroque name of buckminsterfullerene. Not only is this substance remarkable for all sorts of reasons, but the story of how it was identified and created is also well worth recounting. It shows how important scientific advances can come about in unexpected ways, and gives one of the best illustrations of why the often mundane task of molecule-building can occasionally inspire in its practitioners the most feverish excitement. The buckminsterfullerene story shows chemical research at its most colorful.

You will forgive me, I hope, for saving the story for the chapter's climax. In order to understand it better, we will first need to know a little more about this business of molecule-building. Not the least of the pertinent questions is that of what a molecule actually is. What are chemists trying to convey when they draw a picture like Figure 1.1? What in reality are those balls and sticks?

The stuff of the Universe

Why the world really is an illusion

It has become popular in recent years to draw analogies between modern physics and Eastern philosophies such as Taoism and Buddhism. Although this is a little like comparing two books because their covers are the same color, there *is* a sense in which modern science seems to suggest, like Taoism, that the physical world is but an illusion: it states that, very much contrary to appearances, the most solid of objects is nearly all empty space. If we compressed the Earth, for instance, down to a size in which all this empty space was eliminated, it would fit quite comfortably inside a (presumably extraterrestrial) football stadium. In fact, physicists are now having to ask themselves just how much of that football-field-sized lump of matter may also be empty space, but by that stage what we mean by "space" and "matter" is getting a little unclear.

Surely this qualifies as a remarkable illusion! We are sitting or standing on almost nothing but empty space. We *are* little more than empty space. Yet this book feels solid enough, and the mostly-empty-space of our fingers does not penetrate the mostly-empty-space of the pages. In this, as in many other ways, modern physics seems to be at odds with our everyday intuition. As I suggested in the Introduction, it is chemistry that acts as the go-between. At one end of the scale, chemistry can accept and utilize the description of the world provided by fundamental physics; while at the other, it gives us a very rational and self-consistent description of the way that we perceive matter to behave.

The crucial link-up between these two worlds is made at the level of the atom. For the most part, chemistry treats atoms as if they were tiny yet solid balls of matter which stick together in various arrangements to form the substances of which the everyday world is composed. The phenomena that we experience, be they the glowing of a candle's flame, the growth of a crystal, the browning of toast under the grill or the development of a human being from a single cell, can be described largely in terms of rearrangements in the patterns of bonding between these billiard-ball atoms.

But why, if they are mostly empty space, can chemists regard atoms as though they were as solid as billiard balls (that is, as solid as billiard balls *appear* to be)? What is an atom really like?

Order amongst the elements

The Greek philosophers assumed that all matter was composed of just a few different components mixed in varying proportions. These basic ingredients of matter, called elements, were thought to be fourfold: earth, air, fire and water. (Aristotle posited a fifth element, the aether, as a component of the heavenly bodies, while Chinese alchemists proposed a fivefold group of elements: earth, fire, water, wood and metal.)

By the seventeenth century, natural philosophers had come to recognize that, while many substances could indeed be broken down into apparently more fundamental ones, the four-element picture was inadequate. Not only were the basic, irreducible substances very different from earth, air, fire and water, but there were certainly more than four. Many of the elements turned out to be metals, such as copper, iron, tin and lead. Several others were gases, including hydrogen, nitrogen and oxygen. A few were nonmetallic solids, like carbon (which was found in two elemental forms, diamond and graphite) and silicon. Substances that contain more than one element were named compounds.

Chemists have a shorthand notation for the elements, in which each is represented by a one- or two-letter symbol. Most of these are easy to decipher – hydrogen is represented by H, for instance, oxygen by O, nitrogen by N, nickel by Ni and aluminum by Al. Some are more cryptic, since they originate from a time when the elements were called by different names. Iron, for instance, is denoted by Fe, from its Latin form *ferrum*.

In the nineteenth century the French chemist Joseph Louis Proust and the Englishman John Dalton showed that the ratios of elements in a compound remained the same regardless of how the compounds were prepared. Proust enshrined this observation in a general rule which he called the law of definite proportions. The law can be rationalized by asserting that a compound consists of discrete atoms linked into clusters, called molecules, each of which contains a fixed number of atoms of each element. The idea that matter is composed of indivisible units was first posited by the Greek philosopher Leucippus in the fifth century BC; his student Democritus called these fragments *atomos*, meaning "unbreakable." But only thanks to Proust and Dalton was the atomistic hypothesis truly scientific, in the sense of helping logically to rationalize observed phenomena rather than comprising an *a priori* axiom.

The distinction between elements, atoms and molecules is an important one to get straight. If I talk, for example, about the element oxygen, atoms of oxygen and molecules of oxygen, I mean something different in each case. By an "element" I mean simply the substance, without any reference to an atomistic model; an atom is the smallest indivisible unit of an element; and a molecule is a cluster of atoms joined by chemical bonds.

It is rare to find, under normal conditions (which is to say, at temperatures in the region of room temperature), atoms on their own: usually they will be linked together with others in molecules with a well-defined composition, such as those of water (where one oxygen atom is linked to two hydrogen atoms) or in the oxygen and nitrogen gases which are the principal components of air (where the individual oxygen and nitrogen atoms are joined in pairs) (Figure 1.2*a*). Chemists present the composition

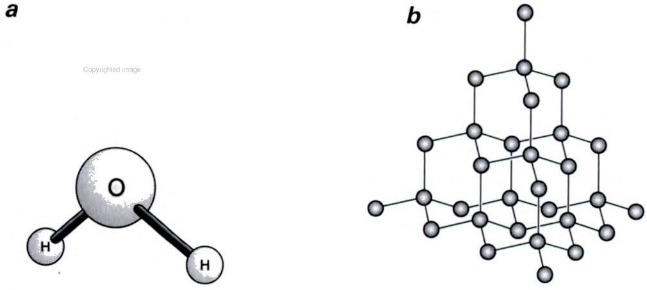


Figure 1.2 *Molecules of nitrogen (N_2) and water (H_2O) (a) and the structure of diamond (b), in which carbon atoms are linked in a continuous crystalline framework.*

of molecules as a "chemical formula" which lists the atoms it contains (in their abbreviated forms). Subscripts denote the number of atoms of each respective element, so that the water molecule is H_2O and the nitrogen molecule is N_2.

In some substances the constituent atoms are not joined into small molecules but are instead linked or stacked together in vast, continuous networks. This is the case in solids such as diamond (Figure 1.2*b*) or metals. There is no reason in principle why we could not consider an atomic network such as diamond to be a single, huge molecule, but it is not generally very instructive to do so. So when I use the term molecule, I will usually be referring to a discrete assembly of atoms of microscopic size, typically containing an easily countable number of atoms. I should mention, however, that we will encounter some molecules that are approaching a middle ground, consisting of perhaps several thousand or even several million atoms.

By the mid-nineteenth century, dozens of different elements had been identified. On the basis of the atomistic model, it was possible to assign each of these elements an atomic weight, which was defined relative to the weight of a hydrogen atom. The actual weight of an atom was a minute quantity and far from easy to measure; but the relative weights of elements were more easily determined. The Italian chemist Amedeo Avogadro suggested in 1811 that equal volumes of two gases at the same temperature and pressure contained equal numbers of atoms (or more precisely, of molecules). The atomic weight of oxygen was therefore the ratio of weights of equal volumes of oxygen and hydrogen gas (this comes out at a value of almost exactly 16).

It was also clear that certain groups of elements had similar chemical properties. The metals sodium, potassium, rubidium and cesium, for example, all react vigorously with water to liberate hydrogen gas. Fluorine and chlorine are both corrosive gases, while helium, neon and argon are all highly inert. The Russian chemist Dmitri Ivanovich

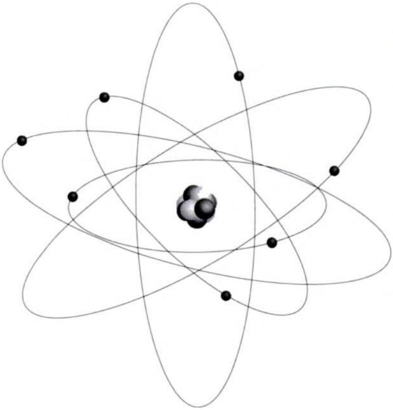


Figure 1.4 *Ernest Rutherford proposed that atoms consist of a tiny, dense, positively charged nucleus orbited by negatively charged electrons.*

atomic number says nothing about the number of neutrons in each atom, however. For small atoms, the neutron count is roughly the same as the proton count – most carbon atoms have six neutrons, for example, and most nitrogens have seven – while heavier atoms tend to have a considerable excess of neutrons over protons. Most atoms of lead have 82 protons and 128 neutrons.

But I emphasize "most" here because the number of neutrons may vary in atoms of any given element. Some carbon atoms have seven neutrons, for instance, and some even eight. They remain atoms of carbon nonetheless, because the atomic number is the same. Atoms of an element that differ in their number of neutrons (and therefore in their overall mass, or ''atomic mass") are called isotopes. The isotopes of hydrogen, popularly called "heavy hydrogen," are deuterium, which has a single neutron in the nucleus as well as a proton, and tritium, which has two neutrons and a proton.

The quantum atom

It would be churlish to disparage Rutherford's "solar-system" model of the atom – it gives an idea of the relationship between the different subatomic components, and it also gives an intimation of how an atom can be mostly empty space. But it should not be taken too literally, because objects this small simply do not behave in the same way as objects the size of the Earth, or even the size of a billiard ball. This is perhaps the central message of quantum mechanics, the theory developed to describe objects at these microscopic scales.

Around the beginning of the twentieth century – even before Rutherford put forward his nuclear model of the atom – physicists began coming across unnerving intimations that there was something very wrong with their "classical" view of the world:

specifically, it appeared sometimes to make incorrect or even nonsensical predictions! The classical theory of electromagnetism formulated in the late nineteenth century by the Scotsman James Clerk Maxwell unified in a beautiful way a great deal of physical science, but unfortunately it also indicated that a hot body should radiate an infinite amount of heat, which was obviously absurd. And existing theories suggested that the speed of electrons kicked out of metals by shining light on them (a phenomenon known as the photoelectric effect) should depend on the intensity of light but not its color, whereas the opposite was found to be the case.

In 1902 the German physicist Max Planck set the stage for the new *Weltanschauung* of quantum theory by hypothesizing that a hot body radiates energy only in discrete packets, called quanta, each of which contains an amount of energy that depends on the wavelength of the radiation. Planck had no particular grounds for making this suggestion, other than the fact that it gave predictions that agreed with experiments. But in 1905 Albert Einstein showed that the same idea can explain the photoelectric effect, suggesting that energy quantization was not merely a mathematical trick but a feature of the real world.

The idea that energy is quantized – that it is transferred in discrete packets – was adopted by Niels Bohr in 1913 to explain the problematic fact that Rutherford's model of the atom contravened the laws of physics as they were then understood. According to the classical viewpoint, an electron orbiting a nucleus should radiate energy constantly until the orbit can no longer be sustained and the electron spirals into the nucleus. The atom would, in other words, be unstable. Bohr suggested that the electrons were restricted to specific orbits, each at a well-defined distance from the nucleus. This implied that the electrons' energies were quantized, and that while it stayed in given orbit an electron's energy remained at a fixed value. Electrons did not radiate energy continuously and spiral into the nucleus because they could increase or decrease their energy only in lumps of specific magnitude.

In Bohr's model of the atom, the allowed energy states of the electrons are like the rungs of a ladder; the spaces in between rungs represent forbidden energies (Figure 1.5).

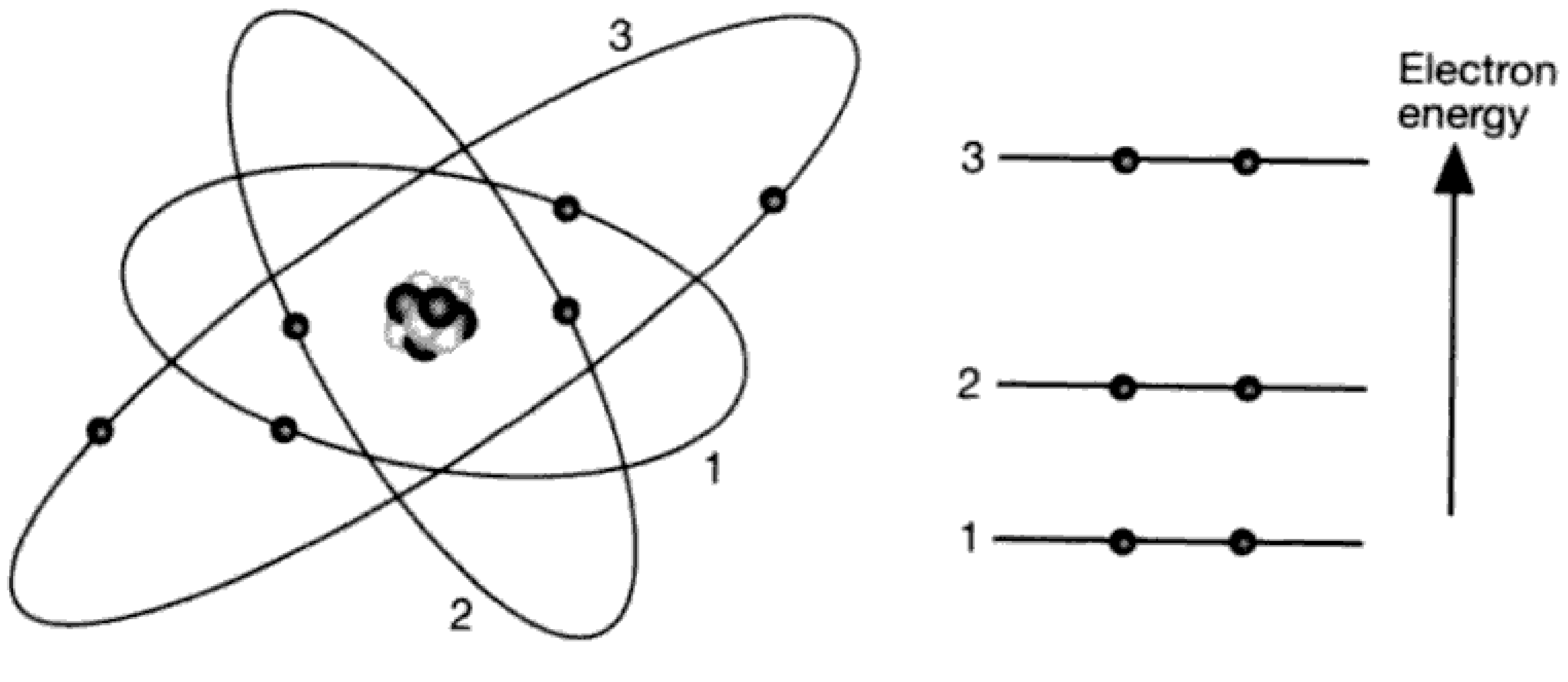


Figure 1.5 *In Niels Bohr's model of the atom, electrons are allowed only specific, discrete energies. They can jump from one rung of the energy ladder to the next, by absorbing or emitting light, but they cannot possess energies in between the rungs.*

Each of these electron "energy levels" corresponds to a certain orbit around the nucleus, so that electrons in one energy level will follow one kind of trajectory whereas those in a different level will follow another. In the Bohr atom these trajectories were still pictured as circular orbits (although the German physicist Arnold Sommerfeld later introduced the possibility of elliptical orbits). But Werner Heisenberg demonstrated in the 1920s that quantum theory would not permit a description of such tiny particles as hard, well-defined objects following line-like trajectories. Rather, at these scales particles get smeared out in a way that prevents one from knowing, at any given time, both their exact position and their exact velocity (or more strictly, their momentum, which is just their velocity multiplied by their mass). In principle we can measure one property or the other as accurately as we like; but as this accuracy increases, the uncertainty with which we can know the value of the other property inevitably increases also. This is one way of expressing Heisenberg's famous Uncertainty Principle, which supplies one of the cornerstones of quantum mechanics. Because of this quantum-mechanical "smearing," one cannot talk about the precise positions of quantum particles but only about the *probability* of finding them at a given point in space.

As a consequence of the Uncertainty Principle, it is more appropriate to think of the electron orbits as corresponding to clouds of smeared-out charge surrounding the nucleus. Where the clouds are dense, there is a relatively high probability of finding the electron. To avoid misleading classical connotations, chemists call these clouds "orbitals" rather than orbits. For the first two energy levels of any atom, the orbitals are spherical – the electrons are more or less localized within a spherical region centered on the nucleus (Figure 1.6). These orbitals, called s orbitals, are therefore not so far removed from the picture of circular orbits, except for the peculiar fact that the electrons do not circulate around the nucleus at all but are instead moving along straight-line trajectories that pass right through it! But the orbitals of the third energy level, which are called p orbitals, are shaped rather like a dumbbell. To simplify again somewhat (although not dangerously), the electrons in these orbitals can be thought of as performing figures of eight through the nucleus. Some of the orbitals with greater energies have shapes that are merely larger version of these two; but others may have still more complicated shapes.

The electronic orbitals come in families or "shells," rather like those of a Russian doll. The first shell contains just one s orbital, denoted the 1s. The second shell has one spherical orbital (the 2s) and three p orbitals (the 2p's), which are arranged at right-angles to each other (Figure 1.6). The third shell has one s orbital (the 3s), three p orbitals (3p) and a group of five d orbitals (the 3d's). The pattern is that each successive shell comprises all the orbital types of the previous shell (but of greater size), plus a new group of orbitals that the previous shell does not possess. The energy of an electron depends both on the shell in which its orbital lies (successive shells correspond to successively higher energies) and, in general, on the nature of the orbital – that is, whether it is an s orbital, a p orbital, a d orbital and so on.

Another important tenet of quantum mechanics, called the Pauli exclusion principle after the Austrian-Swiss physicist Wolfgang Pauli, dictates that each orbital can

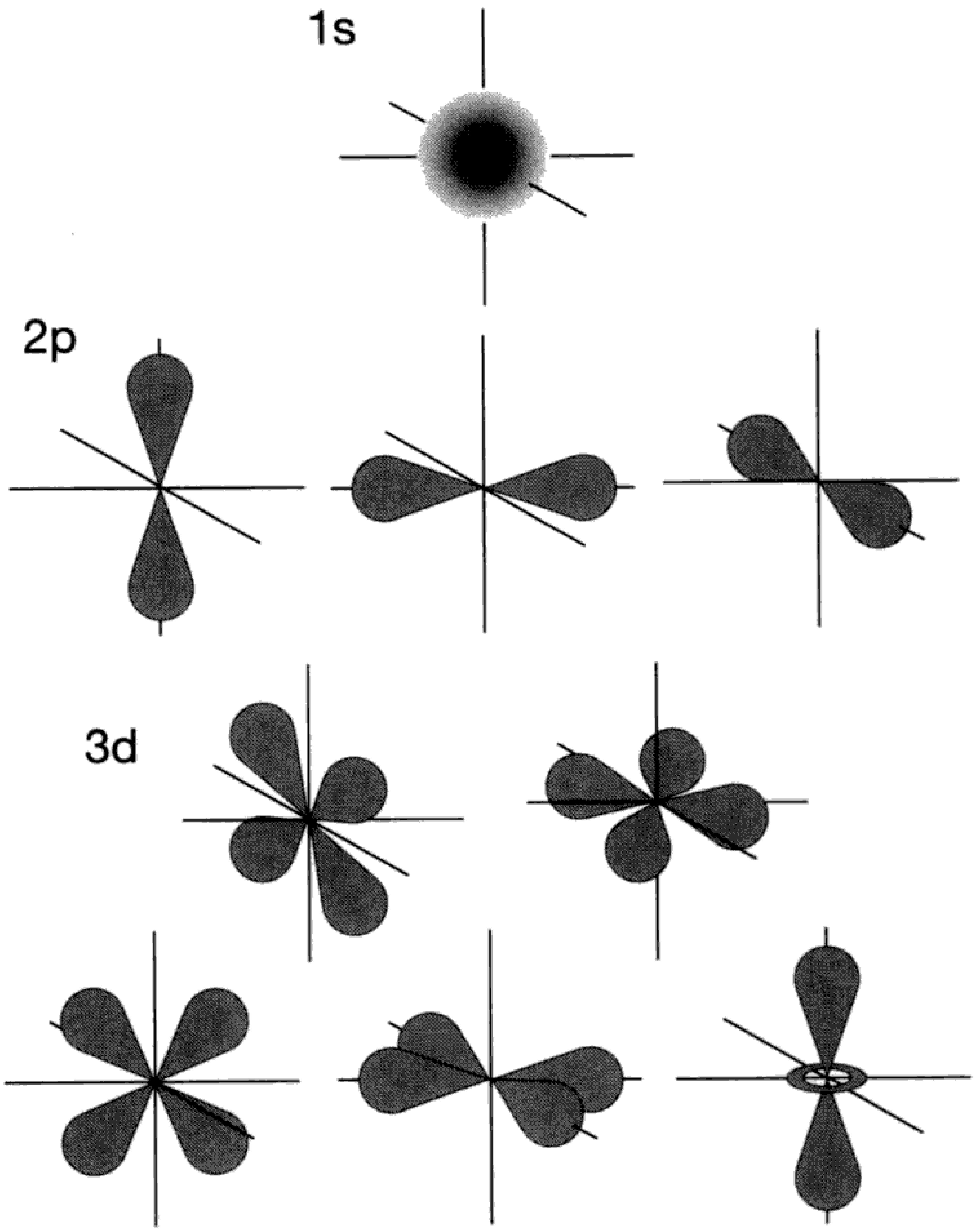


Figure 1.6 *The smeared-out electron orbitals in the quantum atom are very different from the well-defined orbits of Rutherford's "classical" atom. The shaded regions are those in which there is the greatest probability of finding the electrons. The two orbitals of lowest energy (1s and 2s) are spherically symmetric, but the 2p orbitals have a dumbbell shape, and in the third electron shell are orbitals of double-dumbbell and ring-and-dumbbell shapes (3d).*

accommodate just two electrons. Taken together with the shell structure of the orbitals, this provides an explanation for the characteristics of the Periodic Table. The chemical behavior of an atom is determined largely by its outermost layer of electrons. These are sometimes, but not always, those in the orbitals of the outermost shell (the exceptions are the result of orbitals from lower shells "poking through," so that they too must be considered part of the outer layer). An atom's electrons can be considered to "fill up" the orbitals, two to an orbital, from the lowest in energy upwards. So the single electron of the hydrogen atom goes into the 1s orbital, and in helium this electron is joined by another (Figure 1.7). The next element in the table, lithium, has three electrons; two fill the 1s orbital, and the third must go into the second shell. But here it has two choices

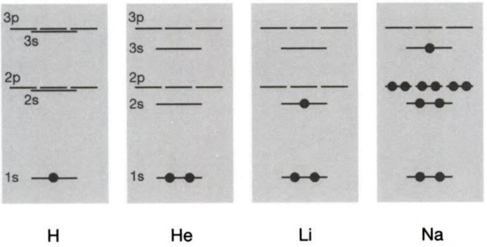


Figure 1.7 *Electrons fill atomic orbitals two at a time, from those of lowest energy upwards. Thus hydrogen has a single 1s electron, helium has two 1s electrons, lithium has two 1s and one 2s, and so on. For hydrogen the energy of the electron levels depends only on the "shell number": the 2s and 2p orbitals lie at the same energy, as do the 3s, 3p and 3d. But for all other atoms this is no longer true. Hydrogen, lithium and sodium all have an outer electron shell containing a single s electron.*

– to go into the 2s or the 2p. For a hydrogen atom, these two orbitals have the same energy, but for any atom containing more than one electron this is no longer true: the 2s is lower in energy than the 2p. So the third electron in lithium goes into the 2s orbital (Figure 1.7). We then go on filling the second shell as the atomic number increases; carbon, for instance, has two electrons in the 1s orbital, two in the 2s, and two in 2p orbitals. By the time we get to neon, with eight electrons, the second shell is full – there are two electrons in the 2s orbital and six in the three 2p's. So for sodium, with nine electrons, the ninth must go into the third shell (that is, into the 3s). This means that both sodium and lithium have an outer shell consisting of one electron in an s orbital (2s for lithium, 3s for sodium) (Figure 1.7), with the result that they tend to react chemically in similar ways. Likewise the outer shell of chlorine is like a bigger version of fluorine's: both have two s electrons and five p electrons (which are in the second shell for fluorine and the third for chlorine). Bromine's outer shell is a yet bigger version of these two.

A new row in the Periodic Table begins each time a new shell starts to be filled. The sudden appearance of a new set of columns after calcium, corresponding to the so-called transition metals (Figure 1.3), signals the point at which the d orbitals begin to be filled. Similar excursions occur after the elements lanthanum and actinium (these are listed outside the main Table to prevent it from getting unmanageably wide), as a result of the filling of yet another new type of orbital in each case.

Atomcraft – the structure of molecules

How the glue sticks

Atoms are linked together in molecules by bonds, which were represented simplistically by sticks in Figure 1.1. Bonds between atoms are formed as a result of their sharing or

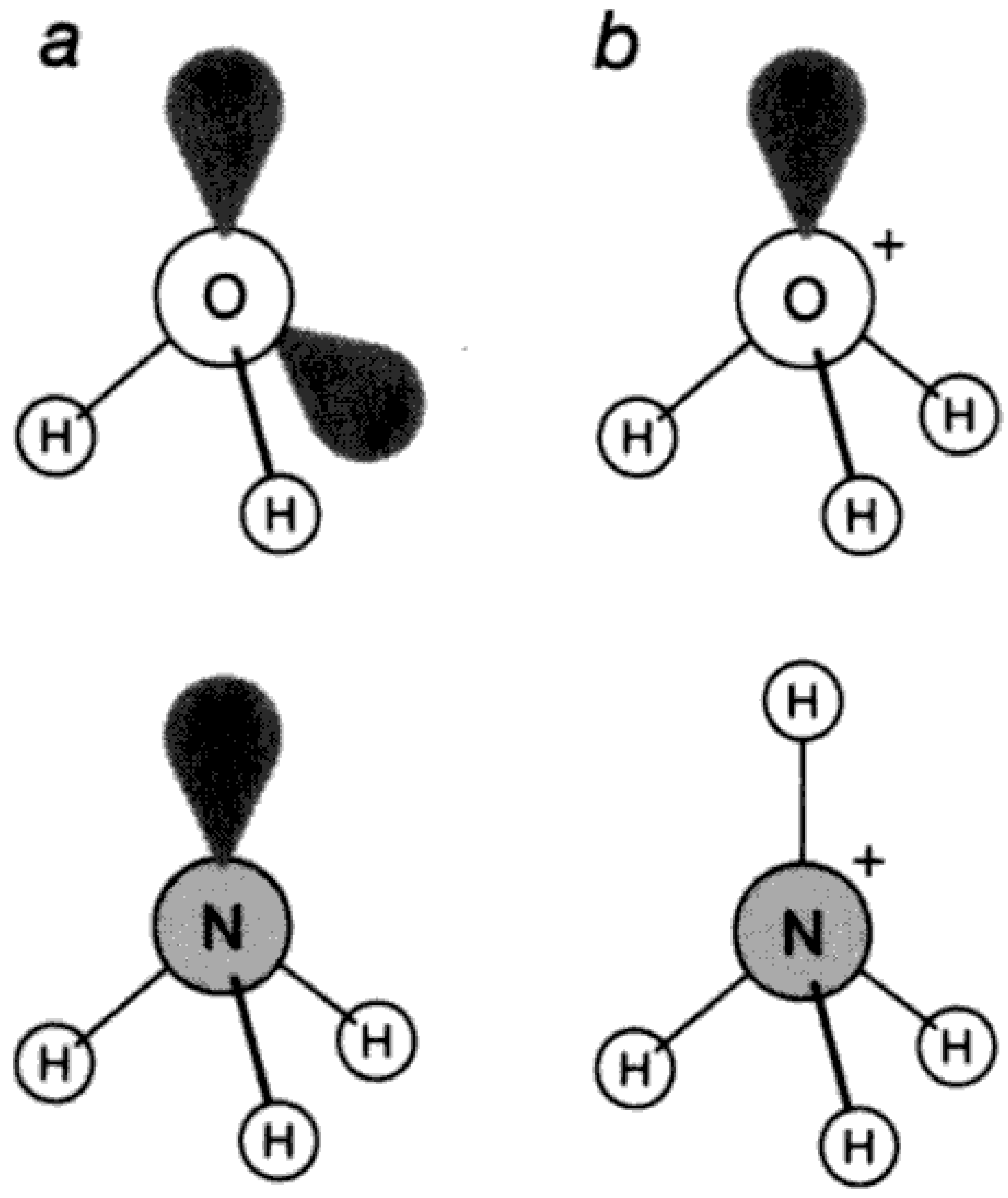


Figure 1.9 *A pair of electrons in an outer-shell orbital that is not involved in covalent bonding represents a lone pair. The oxygen atom in water possesses two lone pairs, while the nitrogen atom in ammonia has just one pair (a). Lone pairs can become involved in bonding with positively charged ions, such as the hydrogen ion, which cannot themselves contribute electrons to the bond. When water or ammonia molecules form an additional bond to the* H^+ *ion, the result is a "protonated" molecular ion (b).*

known as a double bond. These bonds can be considered to have two distinct components: a regular "single" bond (known as a sigma bond) between the atoms in which the electron cloud is densest at the midpoint between the nuclei, and a so-called "pi bond," consisting of two separate, sausage-like electron clouds lying above and below the nuclei (Figure 1.10). Pi bonds are the results of overlap of dumbbell-like p orbitals lying adjacent to each other. One consequence of this structure is that the orbitals of the pi bond act like struts to stop the atoms at each end from rotating: the molecule stays more or less flat.

As one might expect, double bonds are stronger than single ones: to break the carbon–carbon link in ethylene requires more energy than is needed to do the same in ethane (C_2H_6), in which two CH_3 groups are linked by a single bond between carbons. The double bond is, however, considerably less than twice as strong; breaking open the pi component of the double bond is easier than breaking a single bond. For this reason, ethylene reacts with other compounds more readily than does ethane. Carbon compounds that contain pi bonds are said to be unsaturated, meaning that the carbon atoms, while having formed the requisite number of bonds, are not fully saturated in terms of their number of potential neighbors. Saturated carbon molecules, on the other hand, contain only single bonds. The polyunsaturates in oily foods are long, chain-like carbon-based molecules containing many double bonds between carbon atoms. "Saturating" the double bonds by adding hydrogen atoms to them (hydrogenation) yields polysaturates, which have higher melting points. Waxy polysaturated margarines are produced from liquid, unsaturated vegetable oils via this process of hydrogenation.

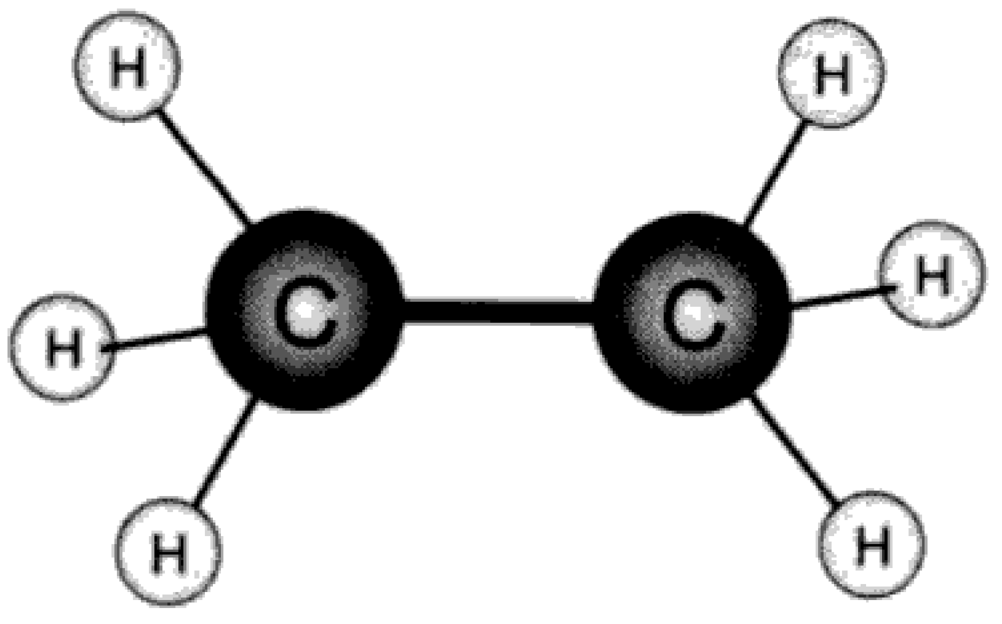
Double bonds by no means represent the greatest length to which atoms will go to ensure that they get their full complement of bonds: triple bonds are also possible. One such is found in acetylene (C_2H_2), in which the two carbons are bound to each other and to just one hydrogen apiece. A triple bond consists of a sigma bond plus two pi

Drawing molecules

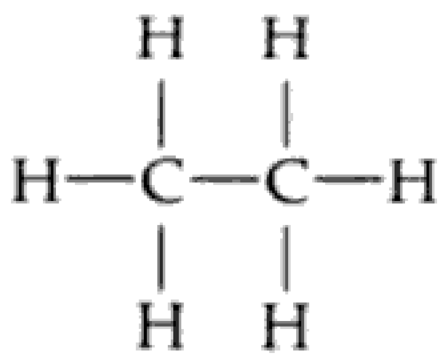
Chemists have several schemes for representing molecular structures. In general these are based on the principle of connecting symbols representing atoms of different elements via lines or sticks that represent chemical bonds. A single line corresponds to a single (sigma) bond, a double line to a double bond and a triple line to a triple bond:

H_2O: H—O—H O_2: O═O N_2: N≡N

Sometimes it is convenient or useful for the positions of the atoms in the illustration to reflect their positions in three-dimensional space; but often this information is not essential. For example, although the three-dimensional structure of the ethane molecule looks like this:

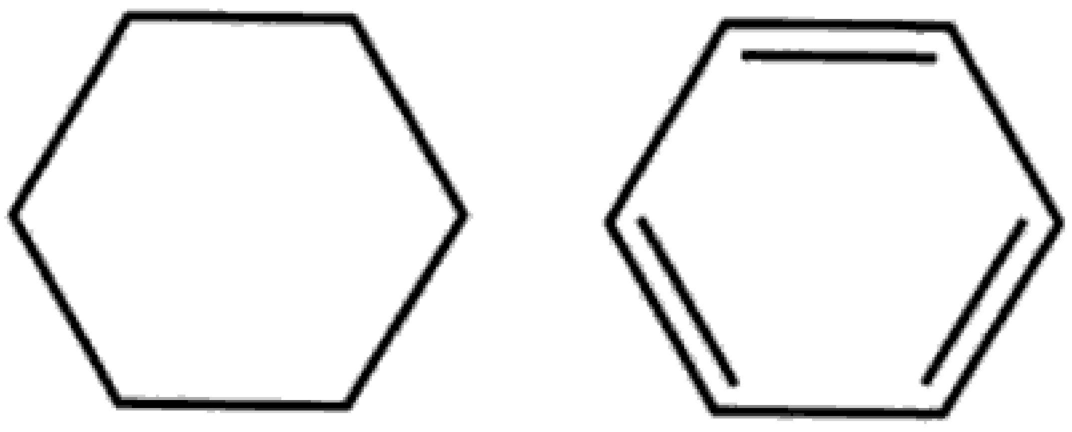


it is generally sufficient to ignore the tetrahedral arrangement of bonds around each carbon atom, and to depict the structure simply as:



$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & - & C & - & C & - & H \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

Because so many molecules are built around a framework of carbon atoms, chemists often use a shorthand notation in which the carbon framework is depicted merely as lines, without the atoms being shown explicitly. The carbon atoms are understood to sit at the kinked vertices of the framework. Because they are very unreactive, the hydrogen atoms attached to carbon atoms are generally an unimportant part of the structure, and so within this shorthand scheme, these hydrogen atoms are omitted entirely for clarity. (Hydrogens attached to oxygen or nitrogen, on the other hand, often play an important structural or chemical role, so they *are* shown.) Thus, within this scheme, cyclohexane (Figure 1.12) and benzene (Figure 1.13) look like this:



Although in reality the cyclohexane ring is puckered, this three-dimensional shape is ignored here.

While ball-and-stick or framework representations of molecules are very good for showing the way in which the atoms are connected, they bear as much relation to the *real* shape of molecules as a stick man does to a human being. Chemists are often more interested in the true, three-dimensional size and shape of molecules, so that they can understand the spatial constraints on the way that molecules interact. This is particularly important, for example, in determining how molecules might stack together with another in crystals. For these purposes, chemists use "space-filling models", in which the building blocks are designed to reflect the effective sizes of the constituent atoms. (As we have seen, atoms don't really have sharp, well-defined edges, but all the same it is possible to ascribe to them an effective radius based on the distance to which other atoms can easily approach.) In space-filling models the atoms are no longer complete spheres, since in a molecule their electron orbitals overlap. A space-filling model of benzene looks something like this:

Here the large gray segments are carbon atoms, and the small black hemispheres are hydrogen.

In this book I will generally show each of the atoms in a molecule as balls. The exception is that, for clarity, I will omit hydrogen atoms attached to carbons in those molecules for which the structures are particularly complicated. When the hydrogens are omitted, I shall indicate as much. If the scale permits, I shall identify the atoms by their chemical symbols, but in large molecules I shall use the code employed in Figure 1.1:

● Carbon ○ Oxygen
◍ Nitrogen ∘ Hydrogen

When it would be redundant or confusing to show the shape of molecules in atomic detail, I will employ more schematic ways of representing their structure – for example, by using the linear carbon-framework scheme or by depicting ring-shaped molecules as a featureless band or rod-like molecules as cylinders.

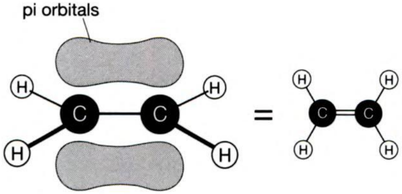


Figure 1.10 *In the ethylene molecule, two carbon atoms are joined by a double bond. One component of the bond is formed from atomic orbitals on carbon which overlap in the region between the two nuclei; this part is called a sigma bond. The other component of the double bond is created by overlap of the two lobes of dumbbell-shaped 2p orbitals on carbon above and below the plane of the molecule, forming two sausage-like electron clouds. This is called a pi bond. In ball-and-stick diagrams, a double bond is represented by two "sticks."*

bonds, in which the sausage-like pi orbitals lie at right-angles to the other (Figure 1.11). Triple bonds are extremely strong, but in carbon compounds they are also very reactive. Acetylene's explosive nature is an indication of this – oxygen molecules will react with it very readily, bursting the triple bond open and releasing the energy bound up in it. This is what happens in the flame of an oxyacetylene blowtorch. But this reactivity is not necessarily the rule in other molecules. The nitrogen molecule (N_2), for instance, has a triple bond between its constituent atoms that is highly stable, which is why nitrogen gas is extremely inert.

In recent years it has become apparent that even higher-order multiple bonds are possible. The ultimate member of the two-carbon molecules, C_2, which contains a quadruple bond, is highly unstable and reactive, but relatively stable quadruple bonds have been identified between two metal atoms.

Full circle

Carbon is the most versatile of atomic building blocks. Its ability to bond strongly to other carbon atoms (via single, double or triple bonds) gives rise to all manner of

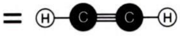


Figure 1.11 *In the acetylene molecule, two carbon atoms are joined by a triple bond. This consists of a sigma bond and two pi bonds, at right angles to one another.*

molecular frameworks, some of which constitute the skeletons of the complex biochemicals, such as fats and steroids, found in living organisms. It should come as no surprise, therefore, that carbon is particularly valuable to synthetic chemists intent on designing molecules with new and unusual shapes. While these molecules have (as we shall see) a tendency to bring out the frivolous natures of their creators, the ultimate motivation for their synthesis may be far from whimsical. The design of molecules with peculiar geometries may be driven by the expectation that they will have useful chemical properties; equally, however, it may represent a dive into uncharted waters. An unusual shape may bestow on a molecule properties unguessed of, or provide insights into apparently unrelated areas of chemistry.

The basis of almost all of the work on unusual carbon molecules is the carbon ring. Hydrocarbons containing rings of five, six and (to a lesser degree) still more carbon atoms are found naturally in petroleum. The six-atom ring is the basis of cyclohexane, in which each carbon is joined to two others and to two hydrogen atoms. The most comfortable arrangement of bonds around each carbon is one that causes the ring to buckle (Figure 1.12).

In an important modern industrial process, a hydrogen atom is plucked from each carbon in cyclohexane to produce benzene (C_6H_6). The discovery that benzene (which is also found naturally in crude oil) is a carbon ring is usually attributed to the German chemist Friedrich August Kekulé, who reported it in 1865; but in fact another German, Johann Loschmidt, seems to have published the ring structure four years before. Legend has it that Kekulé's insight came to him in a dream, in which he had visions of a snake with its tail in its mouth. But as this story seems to have arisen 25 years after Kekulé's "discovery," it is hard to give it much credence. Indeed, some suggest that Kekulé's supposed insight may have actually derived from a glance at Loschmidt's book!

All the same, it is unlikely that the alternating arrangement of single and double bonds around the six-carbon ring will ever become known other than as the "Kekulé structure." There are two equivalent ways in which these bonds can be arranged (Figure 1.13); but if this equivalence is removed, for example by replacing two adjacent hydrogens by chlorine atoms (giving dichlorobenzene), one might expect two distinct structures for the molecule, one with a double bond between the chlorine-bearing carbons and the other with a single bond in this position. Experimental studies insist, however, that there is only one kind of dichlorobenzene. Kekulé proposed that the bonds in the benzene molecule oscillate rapidly back and forth between the two arrangements. The

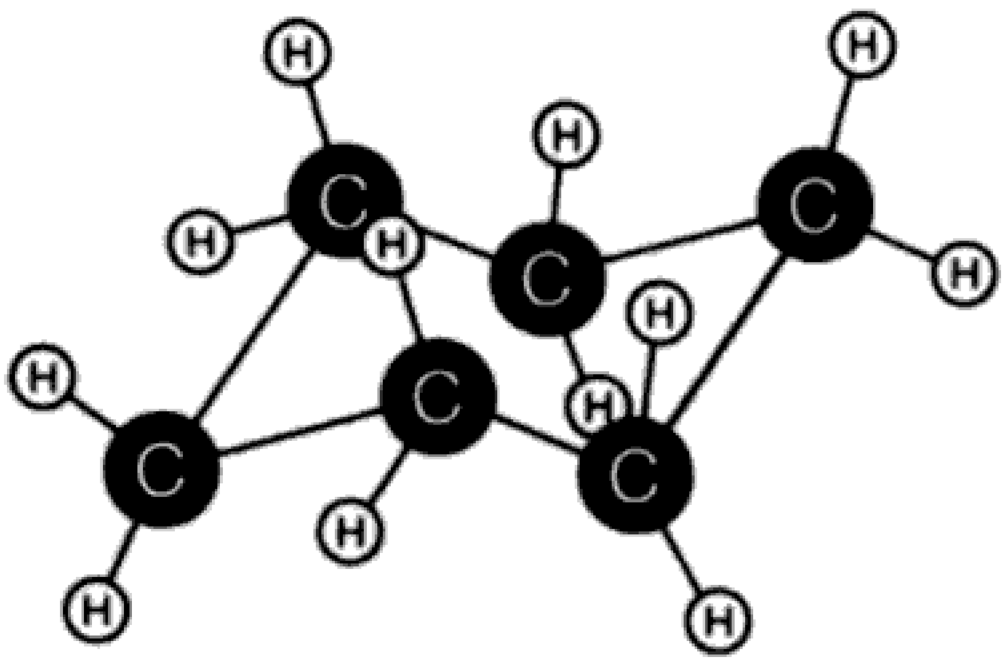


Figure 1.12 *Cyclohexane is a hydrocarbon in which six carbon atoms are joined in a ring. The ring puckers to allow the most favorable arrangement of the four bonds around each carbon atom.*

Building with carbon

The versatility of carbon as a structural element in natural compounds has encouraged chemists to attempt to construct all kinds of audacious molecular edifice. One suspects that the part which chemists relish most is not so much seeing their weird and wonderful molecules take shape, but thinking up names for them. It is perhaps unfair, though not entirely implausible, to imagine that some of these painstaking synthetic procedures have been devised solely because their architects have thought up an amusing name for the intended product!

Carbon rings are the central component of most of these molecules. To create just about any interesting kind of framework structure one needs more than one ring (making the molecule "polycyclic"). The simple example of a four-carbon-atom ring abutting a three-atom ring gives an indication of the way that the name game is played: it is called "housane," and Figure 1.16 shows why. The "-ane" ending reflects the fact that the hydrocarbon is saturated (contains no double or triple bonds), and therefore belongs to the class of compounds called alkanes; the number of bonds on each carbon is made up to four with hydrogen atoms. Both three- and four-carbon rings are said to be strained because the bonds between carbons have to be bent severely to get the ends to join up.

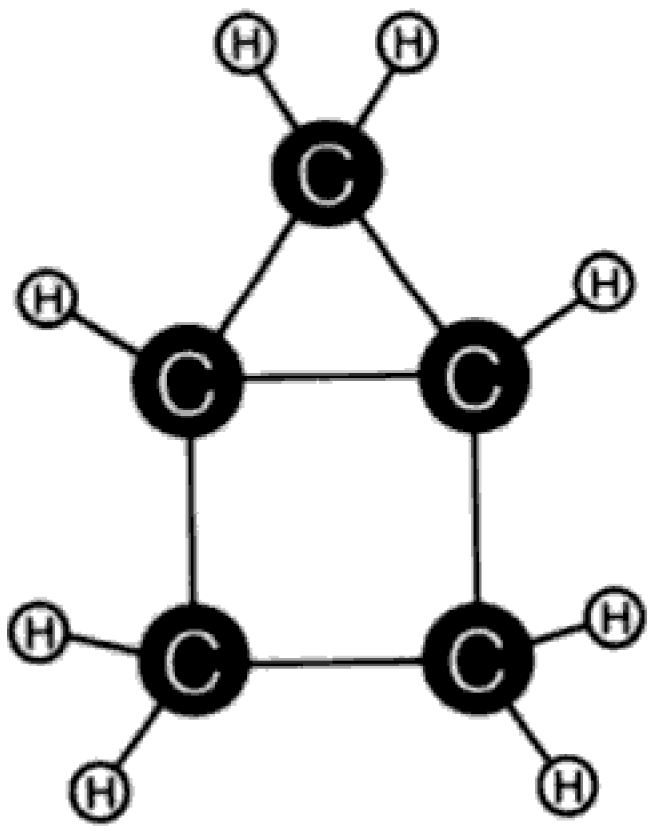


Figure 1.16 *A four-membered and three-membered carbon ring joined together form the housane hydrocarbon.*

If three rings are joined along a common edge, the result is a kind of molecular propellor, therefore inevitably christened a "propellane." But when Jordan Bloomfield of the University of Oklahoma made the first propellane in 1966 (Figure 1.17*a*), the journal editors (a notoriously conservative breed) forced him to relegate the nickname (which he actually formulated as "propellerane") to a footnote. It was David Ginsberg of the Israel Institute of Technology who first got away with using "propellane" for his own variant (Figure 1.17*b*). Kenneth Wiberg of Yale University in Connecticut and colleagues later produced a very unlikely propellane in which three three-carbon rings were joined back to back (Figure 1.17*c*). Joining rings by corners rather than edges takes us from propellors to paddle wheels, which have been christened "rotanes" (Figure 1.17*d*).

The benzene ring provides a flat, disk-like unit with which some researchers have amused themselves by stacking them like dinner plates. The archetypal motif for these

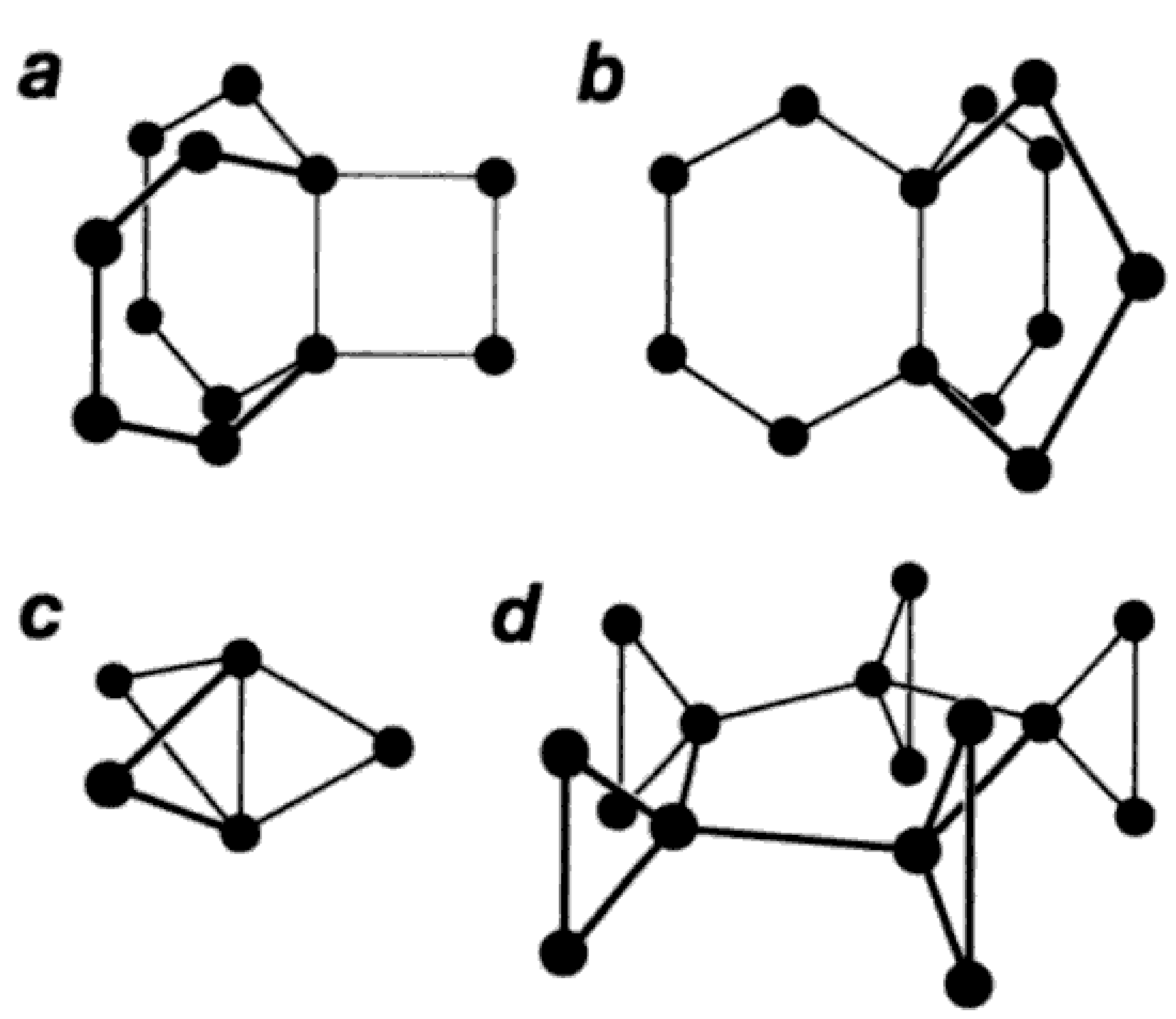


Figure 1.17 *Carbon rings linked edge-on and by corners give rise to propellanes (a–c) and rotanes (d), respectively. Hydrogen atoms not shown.*

stacked molecules is cyclophane, in which two rings are clipped together by short hydrocarbon chains (Figure 1.18). Two or even three pairs of linking struts can be attached, in the latter case producing a molecule that looks like two spiders embracing. Synthesized for the first time in 1979 by Virgil Boekelheide of the University of Oregon, it goes by the name of superphane. An Oriental beauty can be discerned in the remarkable cyclophane made by Masao Nakazaki and colleagues of Osaka University (Figure 1.18); indeed, it reminded them of a traditional kind of Japanese lantern called a *chochin,* and in a break from the conventional suffix they adopted this name as it stood. These cyclophanes are not built for their attractiveness alone, however – some serve as the basic structural units of molecules that can mimic aspects of the behavior of the important natural compounds called enzymes.

More complicated polycyclic hydrocarbon networks can be made by joining rings along more than one edge.

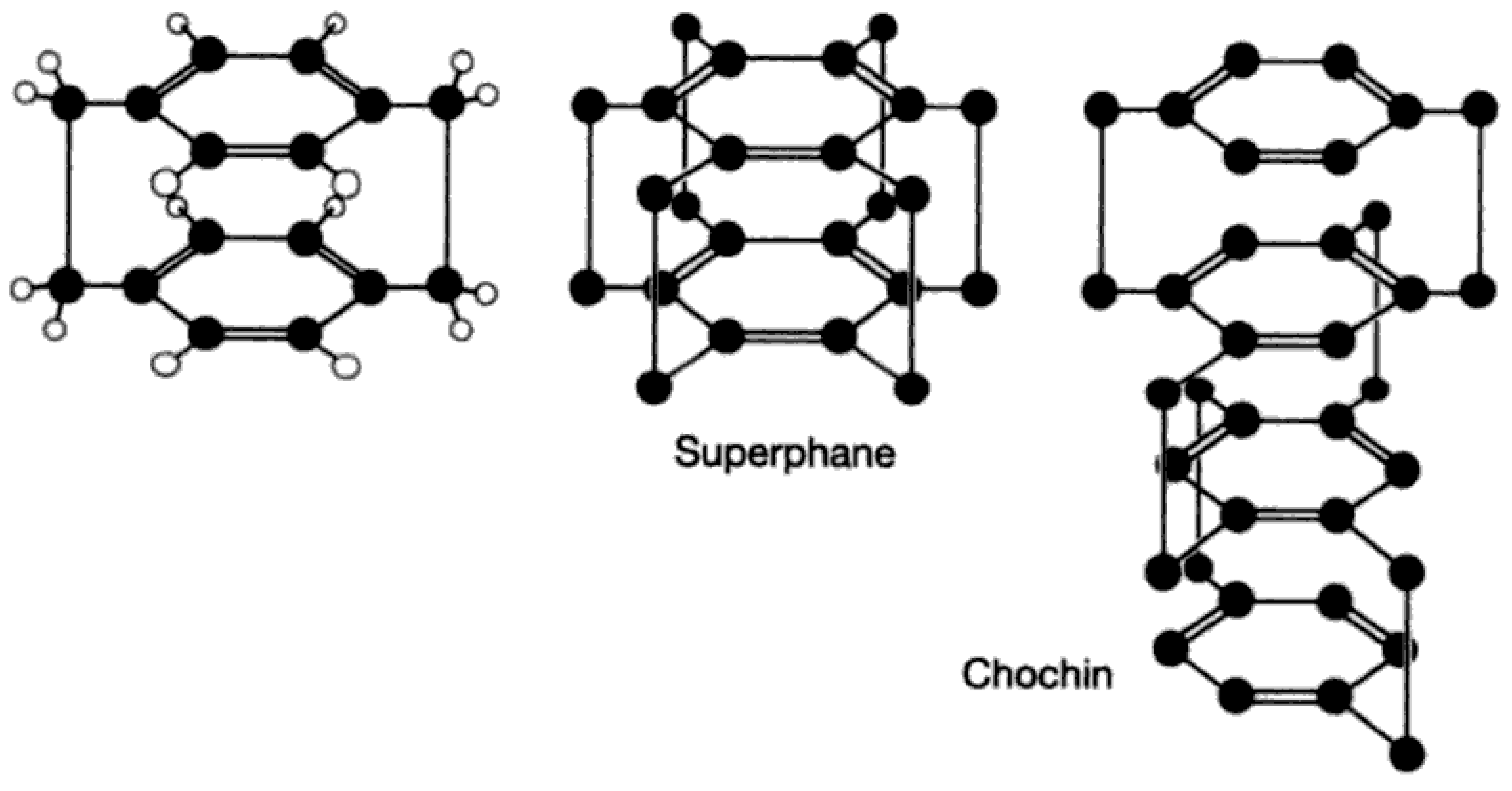


Figure 1.18 *Cyclophanes are benzene rings stacked atop each other, linked by short hydrocarbon chains. Hydrogen atoms not shown in superphane and chochin.*

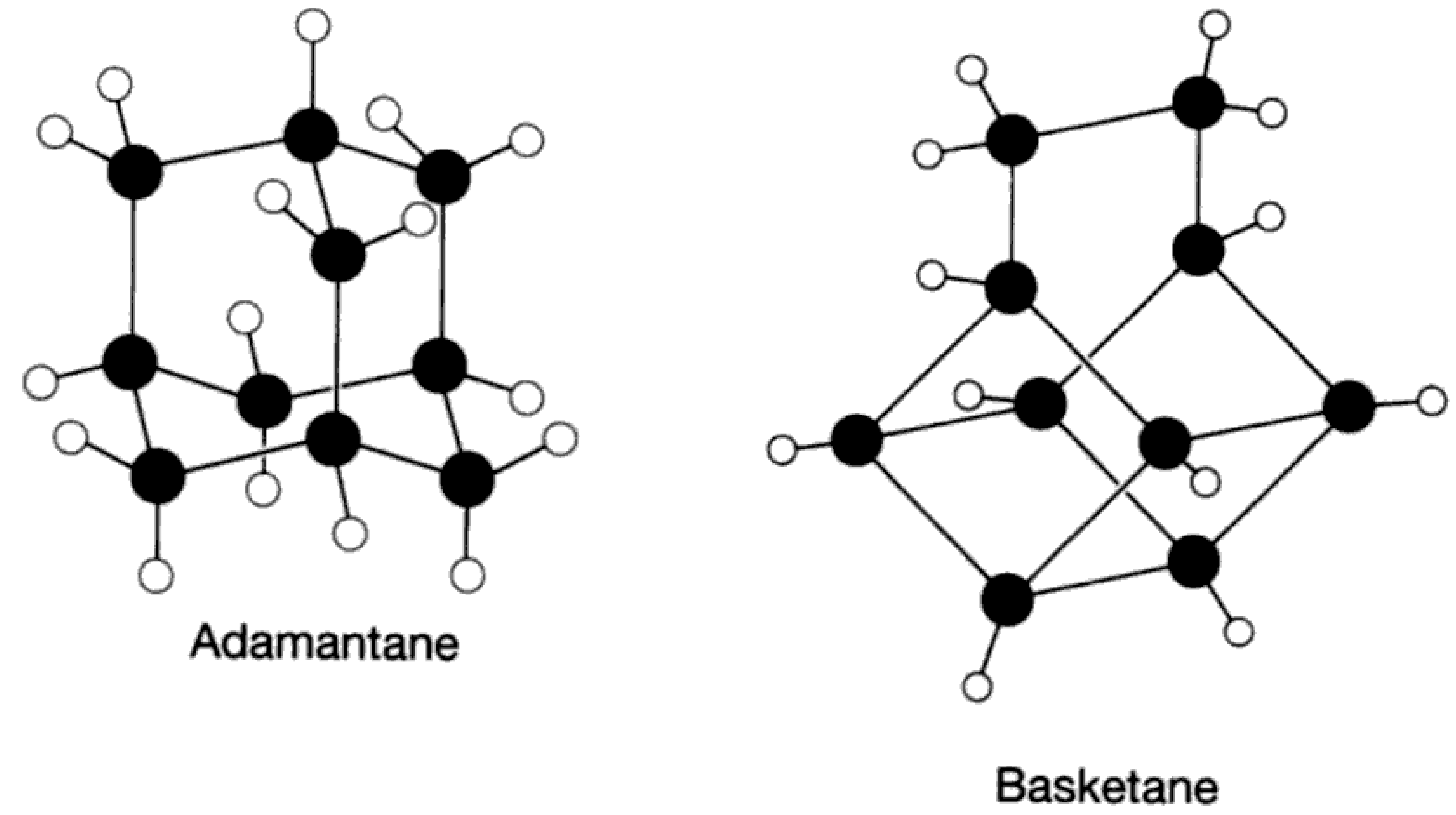


Figure 1.19 *Adamantane and basketane contain several carbon rings joined along their edges.*

The molecule adamantane, shown in Figure 1.19, can be regarded as a fragment cut out of the carbon network of diamond (Figure 1.2*b*). This remarkable molecule was discovered in 1933 by the Czechoslovakian chemists S. Landa and V. Machacek, who isolated it from petroleum. The name is derived from the Greek *adamas,* meaning diamond.

The void inside the adamantane framework makes it a kind of molecular cage. A more obvious hydrocarbon receptacle is the aptly named basketane (Figure 1.19). Basketane is very closely related to a structure that has long fascinated chemists, the perfect hydrocarbon cube. This molecule, called cubane (what else?), was first made by Philip Eaton and coworkers at the University of Chicago in 1964. It is just one member of a whole family of prism-shaped hydrocarbons called the prismanes (Figure 1.20). The pentagonal prism competes with the simpler two-ring molecule mentioned earlier for

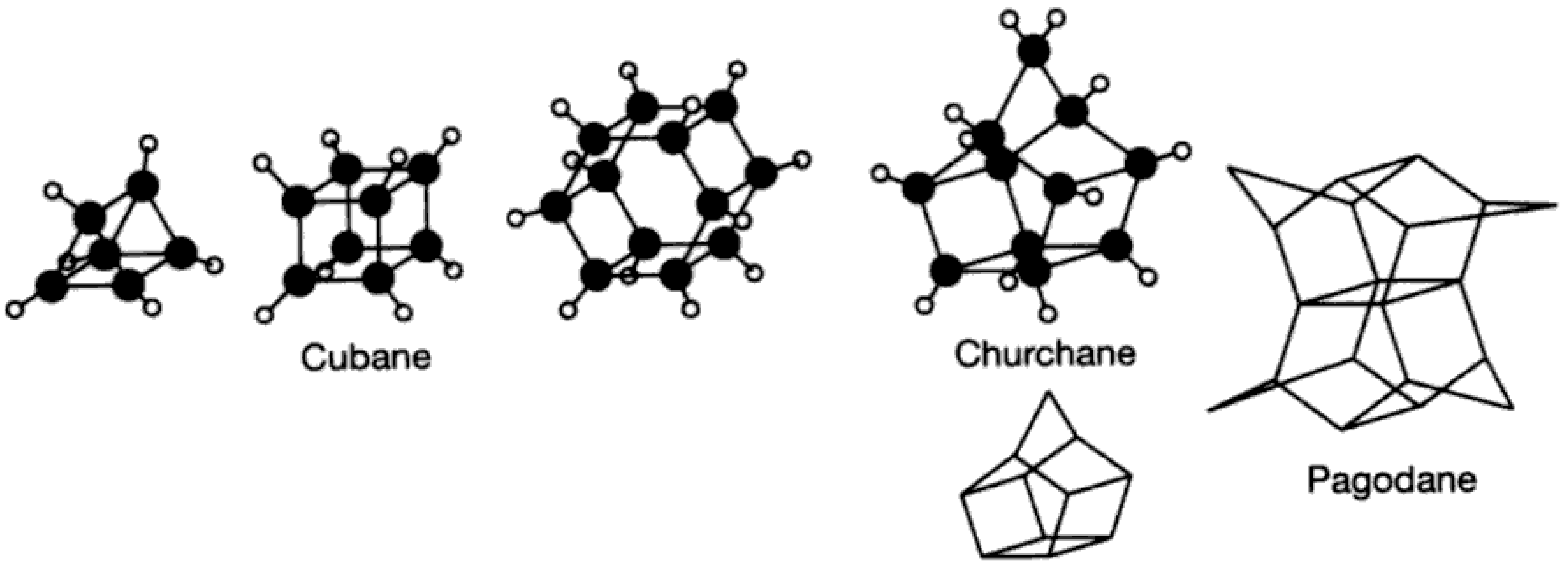
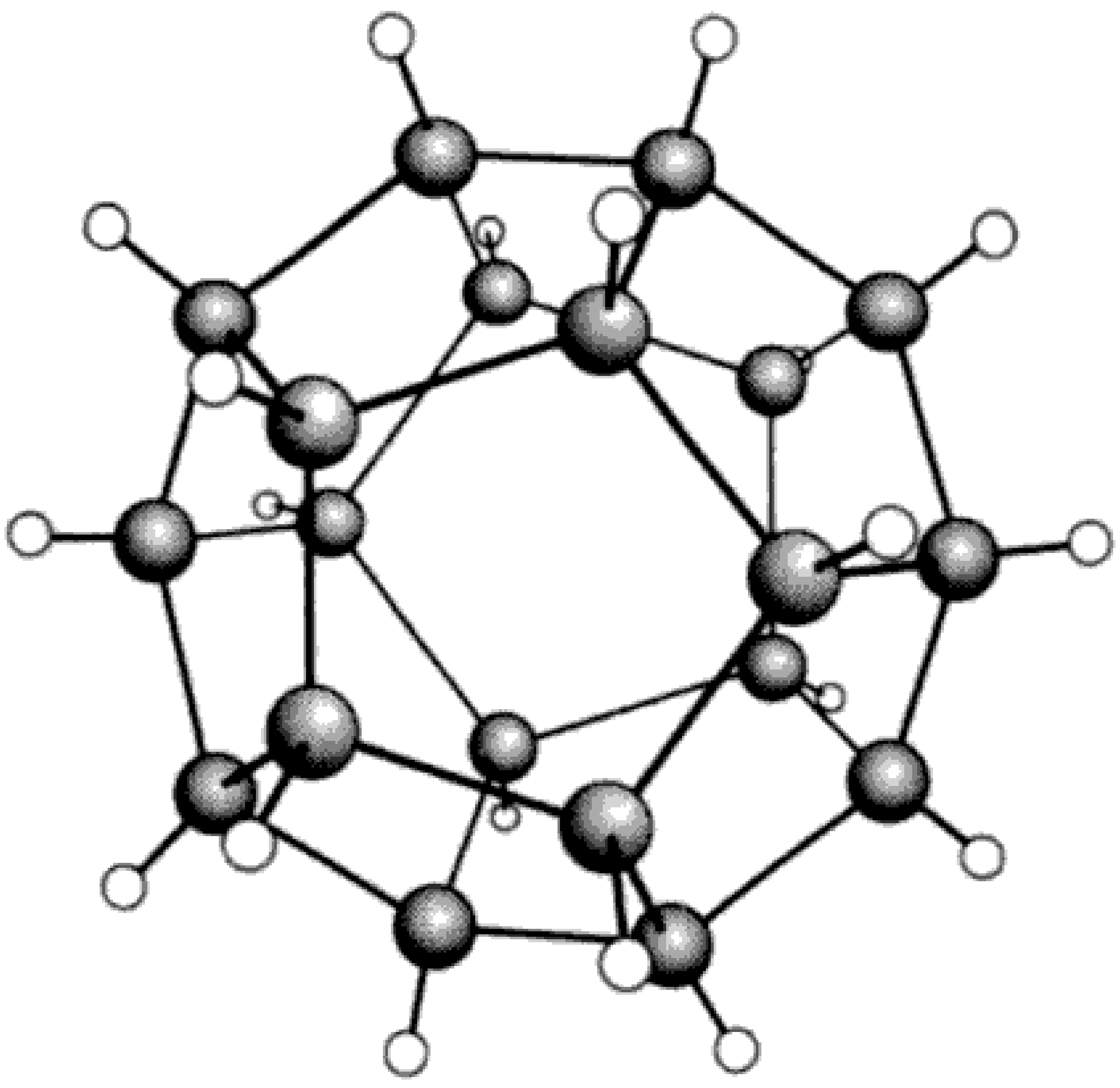


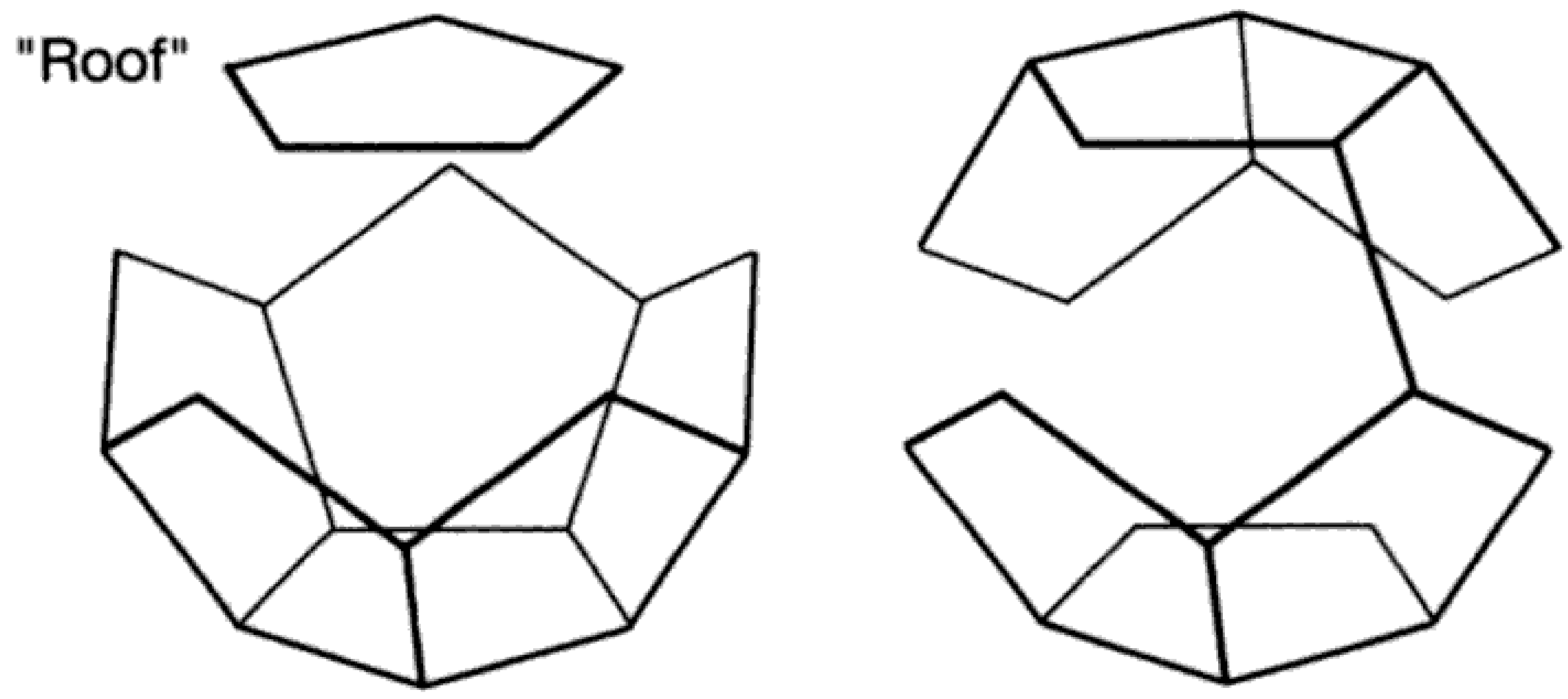
Figure 1.20 *The prismanes are hydrocarbon polyhedra; one of the most well studied is cubane. More ornate variants are churchane and pagodane. For the latter two I show here the carbon framework in "stick" form.*

the name of housane; Gerald Kent of Rider College in New Jersey was moved to add a steeple to this molecular domicile to produce churchane, while Horst Prinzbach and colleagues of the University of Freiburg proposed that the ornate edifice which they built in 1983 from two churchane-like units should be christened pagodane.

As you might imagine from all of this, synthetic chemists cannot resist a challenge. One such, however, presented so daunting a prospect that it remained unconquered by several decades of assault, thereby earning a reputation as "the Mount Everest of polycyclic chemistry." This refractory item is a dodecahedron built from carbon – dodecahedrane (Figure 1.21). Two groups in the 1970s came within spitting distance of cracking the problem, but neither could find a way to make the final links. Philip Eaton's team in Chicago built half of the molecule in 1977, a bowl-like structure of six pentagons. All this needed was a cyclopentane roof linked to the five corners of the rim; with this in mind, Eaton called the bowl molecule peristylane, from the Greek *peristelon,* a group



Dodecahedrane



Peristylane

Bivalvane

Figure 1.21 *The dodecahedrane molecule is one of the most spectacular hydrocarbons synthesized to date. It consists of a perfect dodecahedron of carbon atoms, each capped with hydrogen. Philip Eaton's group couldn't quite manage to put the roof onto peristylane to create the molecule in 1977, but Leo Paquette had more success in 1981 by sealing shut the jaws of bivalvane.*

of pillars designed to support a roof. But they couldn't fix the roof in place. At Ohio State University, Leo Paquette took a different approach: he created two smaller, three-pentagon fragments of the dodecahedron, which were linked via corners (Figure 1.21). This produced a molecule shaped like a clam or a bivalve, suggesting the name bivalvane.

It was not until 1981, however, that Paquette and his coworkers managed to get the clam to close. Their first version of dodecahedrane had the slightly untidy feature of two methyl (CH_3) groups sticking out of it; this compound was a solid with the highest melting point known for any hydrocarbon (greater than 450 degrees Celsius). But by 1982 Paquette's group had tidied up their act to produce the genuine article – perfect dodecahedrane.

Chemistry comes round

It came from outer space

The construction of dodecahedrane represents a pinnacle of achievement in chemical synthesis. It was the product of a long and intricate series of steps in a procedure that utilized the knowledge accumulated over decades of work on carbon compounds. But this elegant molecule has now been eclipsed utterly by one more remarkable still, yet which has been created in a variety of ways so crude that they scarcely warrant description as syntheses at all.

While, moreover, dodecahedrane is strictly a laboratory curiosity whose value resides in a symbolic demonstration of the prowess of modern chemistry, the newest and most stunning of exotic carbon structures promises many practical applications and has already acquired a dedicated field of research all of its own. The study of this molecule is conducted not only by chemists but by physicists, astrophysicists, materials scientists, engineers and biologists. Entire conferences have been devoted to it, newspaper articles and television programs have expounded its virtues. In molecular terms, it is undoubtedly a superstar.

This molecule is a new, hitherto unknown form of pure carbon. As such, its discovery engenders in chemists not a little humility, since they have tended to assume that the natural states of the pure chemical elements were rounded up long ago. Even hoary old chemistry texts that dwell on how to prepare "sal ammoniac" are on sure enough ground when they come to describe the yellow crystals of natural sulfur, the dull gray powder of pure silicon or the pungent green gas that is chlorine. And as for carbon – its natural states diamond and graphite have been known since pretty much the beginnings of civilization. As Joseph Conrad said in 1914, "every schoolboy knows [that there is] a close chemical relation between coal [for which, crudely, read graphite] and diamonds." Yet even today, when schoolgirls too may be familiar with the structure of DNA, it seems that we did not know everything about pure carbon. How is it that a third form of this element passed undetected for so long?

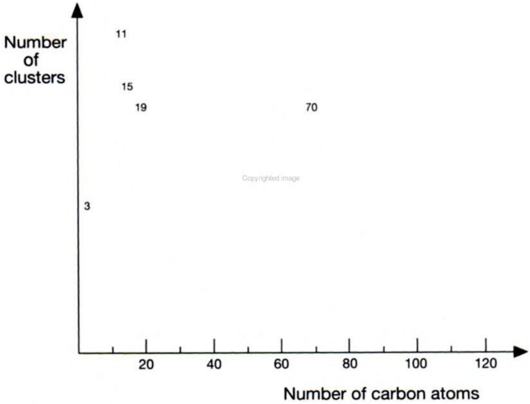


Figure 1.23 *The mass spectrum of carbon clusters produced by researchers at Exxon in 1984. For clusters with more than forty atoms, there is a clear preference for those with even numbers of atoms.*

fully expected to spend "no more than a week or so" working on graphite – for all the intrigue of the astrophysical implications that Kroto foresaw, it was hard to regard the work with anything like the urgency that adhered to the studies of semiconductor clusters.

Kroto and the Rice team first studied the molecules produced when the carbon clusters produced by vaporizing graphite were allowed to react with gases such as hydrogen, oxygen and ammonia, which might be expected in carbon-star atmospheres. They found the cyanopolyynes that Kroto had expected, along with other chain-like molecules. The mass spectra from graphite alone, meanwhile, were very similar to those that the Exxon group had described: here again was the rather mysterious preference for even-numbered clusters above about forty atoms. After several experimental runs, however, something became apparent in these spectra of which the Exxon report had made no mention: the peak corresponding to a sixty-atom cluster was sometimes appreciably – as much as three times – larger than those to either side. It seemed that formation of the sixty-atom cluster, denoted C_{60}, was at times more favorable than the formation of the other even-numbered clusters (Figure 1.24). In fact, the Exxon group had noticed this result too, but because they had no explanation for it they had made no mention of it in their paper.

On the afternoon of Friday September 6th, Kroto and the Rice team decided that they should try to identify the experimental conditions under which the sixty-carbon peak was most prominent. Heath and O'Brien were more than happy to sacrifice the weekend for the possibility of uncovering a new result, and offered to spend the two

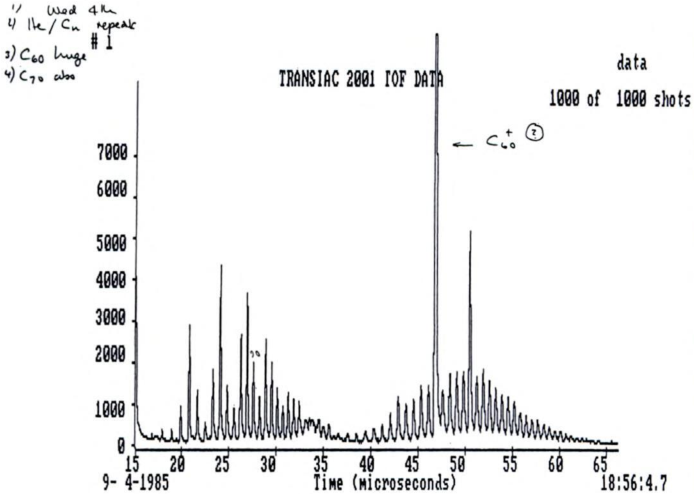


Figure 1.24 *In the mass spectrum of laser-vaporized carbon obtained by Harry Kroto and Richard Smalley's group at Rice University, the peak corresponding to the sixty-atom carbon cluster (C_{60}) stands out loud and clear. In this plot – the raw data from one of the early runs – Harry Kroto picked out the most prominent peak with a tentative "C_{60}^{+}?," and the researchers noted in the corner that the peak presumably due to C_{70} is also clearly evident to the right. (Picture courtesy of Harry Kroto, University of Sussex.)*

days trying to adjust the experimental conditions so as to identify how to enhance the formation of C_{60}. On the morning of the following Monday they revealed the fruits of these efforts: mass spectra in which the C_{60} peak was like a mountain surrounded by little hillocks. At the same time the seventy-atom cluster (C_{70}) was also prominent – it seemed to recur as an inseparable companion to the huge C_{60} signal.

The researchers set about trying to figure out how it was that C_{60} came to be so much more stable than the other clusters. There must be, they decided, something about its structure that would account for this stability. For these large clusters, a chain structure was most unlikely. An alternative candidate was a graphite-like structure in which the carbon atoms were bonded into small flat sheets stacked one atop the other. Kroto suggested that a symmetrical arrangement of C_6, C_{24}, C_{24} and C_6 sheets would explain the magic number 60 (Figure 1.25). But all such structures leave the carbons at the edge of the sheets with just three bonds apiece, rather than the requisite four, giving them an unsatisfied "dangling" bond; this would be likely to make the cluster very reactive.

Figure 1.25 *Attempts to construct a C_{60} cluster from graphite-like layers of carbon hexagons leave "dangling bonds" at the edges, which would make the clusters highly reactive. This version, postulated by Harry Kroto, was nevertheless somewhat appealing as it suggested a possible interpretation of the preference for 60 carbon atoms: a quadruple-decker sandwich of 6, 24, 24 and 6 carbon atoms. But Kroto and his colleagues were to dream up a more startling alternative for the sixty-atom structure.*

One way of getting around the problem of dangling bonds would be to have the sheets curl up on themselves to form closed shells. Although this was a promising idea, it wasn't clear how a graphite-like sheet of carbon atoms, which is perfectly flat, could be induced to bend. For Kroto, however, these curved hexagonal sheets awoke memories. In 1967 he had visited the Montreal Expo exhibition and become captivated by the US Pavilion, designed by the American architect Richard Buckminster Fuller. It was a geodesic dome built from flat polygons (Figure 1.26). Buckminster Fuller was something of a maverick amongst architects, and these domes were a characteristic of his work. Kroto recalled that the Montreal dome had been fashioned from hexagonal units. Could C_{60} be a miniature version of Buckminster Fuller's bizarre designs? But while it was easy to arrange hexagons into a flat sheet, it was not obvious to the researchers how to construct a closed dome.

Figure 1.26 *Richard Buckminster Fuller's geodesic dome at the Montreal Expo of 1967. The dome is made from triangulated polygons joined at their edges. (Photograph by Robin Whyman, kindly supplied by Harry Kroto.)*

A mathematician would have given them the answer immediately: to construct a dome from hexagons is simply not possible. This had been proved in the eighteenth century by the Swiss mathematician Leonhard Euler, and the fact was no doubt known to Buckminster Fuller. Kroto did recall, however, that five-sided shapes – pentagons – might also have featured in the domes. He remembered also a cardboard kit that he had once purchased and assembled for his children, a sphere-like map of the heavens which he called a "stardome." This too had been built from hexagons and pentagons. But none of the researchers was quite sure what the rules were that governed such objects. As Kroto was due to return to England on the Tuesday, there was little time left to solve the puzzle. In the library at Rice, Smalley located a book on Buckminster Fuller's work, *The Dymaxion World of Buckminster Fuller* by Robert W. Marks, which he took home on the Monday evening to ponder.

It is remarkable to find that, despite what we like to think of as the sophistication of modern science, some of the most significant insights can still be obtained by sitting down with a can of beer and fiddling with cardboard or ball-and-stick models. Yet this is how the structure of C_{60} was deduced. That night James Heath collected sixty "Juicy Fruit" gum balls and attempted to stick them together with toothpicks in an effort to model the sixty-atom cluster. Hours later he and his wife had little to show for their efforts but sticky fingers and an empirical awareness of Euler's dictum that a closed shell cannot be made purely from hexagons. Meanwhile Smalley, having abandoned efforts at cracking the problem on his home computer, took to fiddling with cardboard hexagons and sticky tape. His attempts to create from these a curved structure came to nothing, but as midnight came and went he remembered Kroto's comment about pentagons. Once he added these to the makeshift construction kit, everything began to fall into place. Five hexagons arrayed around a pentagon with their adjacent edges touching automatically curl upwards into a bowl (Figure 1.27). On adding further hexagons and pentagons, Smalley was able to produce a hemisphere. The rest was easy: constructing another hemisphere on top produced a ball-like polyhedron containing twelve pentagons and twenty hexagons. Counting corners (where the atoms would sit), Smalley found to his delight that he had built a sixty-atom cluster.

Figure 1.27 *Building a closed cage from hexagons and pentagons. The pentagons are essential to get the sheets to curl up and the cage to close.*

The carbon soccer ball

The dome structure (Figure 1.28*a*) had everything. It was beautifully symmetrical, it was robust, it explained the "magic" number of 60, and it had the pleasing feature that every corner (that is, every atom) was equivalent. How could it be anything other than correct? This was Smalley's view when he called together his colleagues the following morning and showed them the model. They were struck at once by the aesthetic appeal of the solution, but Bob Curl cautioned that the model also had to make sense in chemical terms. Each carbon atom had to have four bonds, and as each was attached to three other carbons, one of those three bonds had to be a double bond. Could one arrange double bonds on the object in such a way as to satisfy this requirement for every atom? Using sticky labels to represent double bonds, Curl and Kroto quickly established that one could (Figure 1.28*b*).

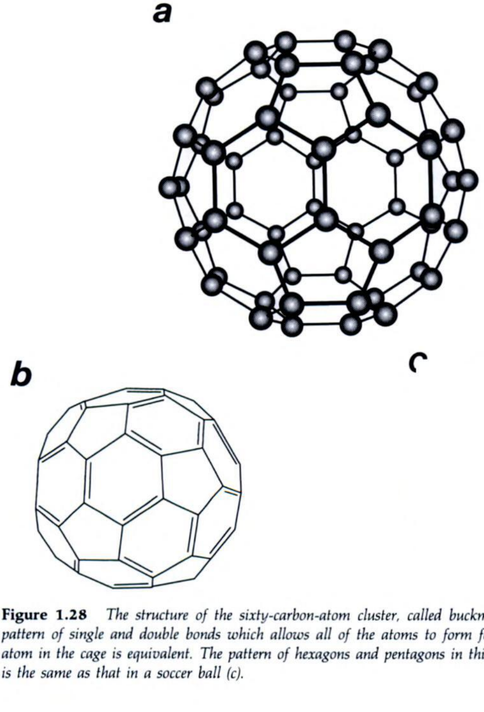


Figure 1.28 *The structure of the sixty-carbon-atom cluster, called buckminsterfullerene (a), and the pattern of single and double bonds which allows all of the atoms to form four bonds (b). Each carbon atom in the cage is equivalent. The pattern of hexagons and pentagons in this highly symmetrical shape is the same as that in a soccer ball (c).*

In 1986 Kroto and the Rice researchers conjectured that, if the fullerenes really were hollow carbon cages bearing a resemblance to graphite, might they not be formed in the soot produced from combustion of carbon-rich substance? Soot is, after all, nothing more than disordered fragments of graphite-like sheets, and fullerenes appeared to represent the perfect way of avoiding dangling bonds at the sheet edges. But combustion chemists seemed unwilling, on the whole, to take up the challenge of looking for C_{60} in soot. When, in 1987, Klaus Homann and colleagues at the Institute of Physical Chemistry in Darmstadt performed a mass spectrometric analysis of the ions formed in sooty flames and found that the most abundant carbon ion with more than ten atoms was that containing sixty, the observation was explored no further, even when Kroto pointed out the possible connection with the experiments at Rice. In those days, either you were a believer or you weren't! Homann's result was recalled in 1991, however, when researchers at the Massachusetts Institute of Technology reported that by carefully controlling the combustion rate and mixture of gases in flames of natural gas ignited in air, they could produce C_{60} and C_{70} in respectable quantities. The implication is that mankind may have been making C_{60} unwittingly for millenia.

Fullerene frenzy

After 1985, buckminsterfullerene acquired something approaching cult status. Everyone had heard of the *Nature* paper but most regarded it as a rather quaint curiosity. Kroto, however, became convinced that the molecule might provide the key to a whole new facet of carbon chemistry. Maybe here was a way to wrap up toxic or radioactive metal atoms in individualized carbon coatings. Perhaps C_{60} would make an excellent lubricant, since the carbon balls might roll over each other like ball bearings. The speculations were many and colorful; but they remained speculations all the same, because the stuff had been produced only in minute quantities, mixed up with all the other products of laser ablation. And because no one had succeeded in isolating significant amounts of the pure material, the experiments that could confirm the hypothetical soccer ball structure remained beyond reach. In 1990, all that changed.

Like Harry Kroto, the physicists Donald Huffman at the University of Arizona in Tucson and Wolfgang Krätschmer at the Max Planck Institute for Nuclear Physics in Heidelberg had in the early 1980s become interested in the possibility that novel carbon molecules might be formed in stellar atmospheres and interstellar space. The two physicists collaborated in 1982 on experiments in which they vaporized graphite by electrical heating and measured the properties of the black soot that was produced. Huffman and Krätschmer studied how this soot absorbed ultraviolet light so as to compare the absorption spectra with those measured by astronomers. They found that their soot behaved much like that produced in ordinary combustion except for some features in the ultraviolet spectrum that were not observed for normal soot. At that time, they concluded that the extra features were due to impurities that had crept into the vaporization chamber, perhaps the oil used in the vacuum pump. It was not until three years after the 1985 *Nature* paper had been published that Huffman realized that perhaps what he and Krätschmer had seen back in 1982 was the signature of C_{60}.

Huffman's idea was received with some skepticism by Krätschmer, but the two agreed that the idea was worth testing further. When Krätschmer's group at Heidelberg measured the mass spectrum of the carbon soot produced by heating graphite with an electrical arc discharge, they saw immediately the prominent C_{60} peak. After some trial-and-error adjustments, the researchers were able to produce C_{60} in relatively large quantities – a few milligrams – with their simple arc-discharge technique. These amounts would certainly be sufficient for the experiments that could establish the structure beyond doubt, but the obstacle that remained was the need to extract pure C_{60} from the rest of the detritus. Early in 1990, Krätschmer, Huffman and their respective students Kostantino Fostiropoulos and Lowell Lamb tried heating the soot so that part of it sublimed; when cooled, the vapor condensed back to a solid. Part of this solid dissolved in liquid benzene to give a deep red solution, and evaporation of the benzene solvent left reddish brown crystals (Plate 1). Mass spectrometric analysis revealed that they contained 90 per cent C_{60}, the remainder being C_{70}. Here at last was the opportunity to put the soccer ball structure to the test. By bouncing X-rays off the crystals (a technique described in Chapter 4), the researchers were able to deduce that the crystals comprised stacks of spherical molecules with their centers about a nanometer (one thousand-millionth of a meter) apart – just what was expected for regular arrays of C_{60} balls. In August 1990, Krätschmer and Huffman described their new method for isolating C_{60} and their evidence for the soccer ball structure in a paper in *Nature*. To Kroto the news of this success came both as a delight and as a bitter blow. It showed that he and the Rice group had guessed right after all in 1985; but Krätschmer and Huffman's breakthrough had beaten his own efforts by a whisker. Kroto had experimented with a similar arc-discharge technique in 1986, but had been severely hampered by a lack of financial backing. He had caught wind of the advances that Krätschmer and Huffman were making in 1989 when they presented a preliminary report of their work at a conference, and had resurrected the arc-discharge apparatus. But he and his colleagues at Sussex faced the same problem of extracting the C_{60} from the soot. By August of 1990 Kroto's colleague Jonathon Hare hit on the benzene separation method independently, and obtained the red solution. But by then the race was already run, since Krätschmer and Huffman had managed the crucial last step of getting crystals out of the solution. When *Nature* asked Kroto to act as a referee of the paper sent by Krätschmer and Huffman he realized that his group had been beaten to the finishing post.

All the same, the Sussex team took advantage of the fact that, with their red solution already to hand, they were at least ahead of other rival groups at that stage. By the end of August they had performed the test that clinched the case for the predicted structure of the molecule – a test that was missing from the paper of Krätschmer and Huffman, although their conclusions could scarcely be doubted for all that. The experiment involved the use of a technique called nuclear magnetic resonance (NMR) spectroscopy, which showed that every one of the sixty carbon atoms is equivalent – just as is predicted for the soccer ball structure. These NMR experiments also confirmed the rugby ball structure of C_{70}.

The jury was in: C_{60} is a molecular soccer ball. Within months of publication of Krätschmer and Huffman's recipe for mass-producing C_{60}, everyone was playing the game. Soon the molecules were to be seen lined up in neat rows under a new kind of microscope called the scanning tunneling microscope (Plate 2). Organic chemists started to explore how C_{60} behaves in chemical reactions. Most theoretical calculations predicted that it would be a relatively stable, unreactive molecule, like benzene. But it turns out to be not so difficult to open up the double bonds in the carbon cage: hydrogen and fluorine, for example, can be attached to the carbon atoms. The balls have been attached to the backbone of long, chain-like polymer molecules, like a string of lucky charms. In an electrochemical cell, C_{60} was found to take up additional electrons to form negative ions such as C_{60}^{-} and C_{60}^{2-}, implying that it should form "salts" with metals, just as if it were an unusually large atom resembling, say, chlorine.

This led researchers at AT&T Bell Laboratories in New Jersey to react C_{60} with the alkali metals lithium, sodium, potassium, rubidium and cesium. While ionic salts were indeed formed, these compounds proved to be far stranger than the researchers had anticipated, as we will see in Chapter 6. It will suffice to say here that these experiments showed C_{60} to be not only the most interesting molecule to have come the way of chemists for many years, but also to have some astonishing revelations in store for physicists too. Compounds of C_{60} and metals now provide one of the main focuses of C_{60} research.

A particularly intriguing variety of these compounds appear to contain metal atoms *inside* the cage. These so-called endohedral ("inside the polyhedron") structures are made by forming fullerenes from a composite of graphite and a metal compound. The first were synthesized by Jim Heath almost immediately after he, Kroto and the Rice team discovered the molecule itself in 1985, by applying the laser ablation method to rods of graphite mixed with lanthanum oxide. They found that individual lanthanum atoms became intimately associated with the C_{60} cage; the obvious corollary was that they were trapped inside. As many as four metal atoms have now been trapped inside a fullerene shell.

The ball keeps rolling

C_{60} has proved so easy to make that countless scientists have been unable to resist the temptation to dabble with it in the hope of uncovering some new and unexpected property. For those who do not want to go to the lengths of setting up their own little C_{60} factory, the molecule and its relatives (C_{70}, C_{84} and so on) are now available in gram quantities from several commercial companies in the United States. It is not exactly cheap at present (about forty times the price of gold), but some expect C_{60} to cost no more than aluminum in a few years time.

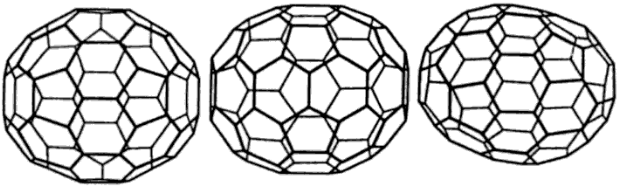


Figure 1.30 *Some of the larger fullerenes, such as C_{76}, C_{78}, C_{82} and C_{84}, have been isolated and their structures deduced. Although in principle a huge number of isomers can be postulated for each, the requirement that no two pentagons be adjacent reduces the range of possibilities to just a few. Here I show some of the structures deduced for the C_{78} molecule.*

For those in search of vistas still more exotic, the properties of many of the larger fullerenes are still largely unexplored. All, it seems, must contain twelve pentagonal carbon rings as predicted from Euler's work. Moreover, while there are in principle a huge number of possible arrangements of the five- and six-membered carbon rings, the situation is greatly simplified by the fact that the five-membered pentagonal rings avoid being placed side by side – this would give rise to an unstable bonding pattern, which would rapidly rearrange. For C_{60}, for instance, there are 1,812 ways of arranging the pentagonal and hexagonal rings, but only one in which no pentagons are adjacent.

Molecules for which the same constituent atoms are arranged differently in space are called *isomers*; we will encounter several examples in the later chapters. The rule that all pentagons must be isolated from one another reduces the number of observed

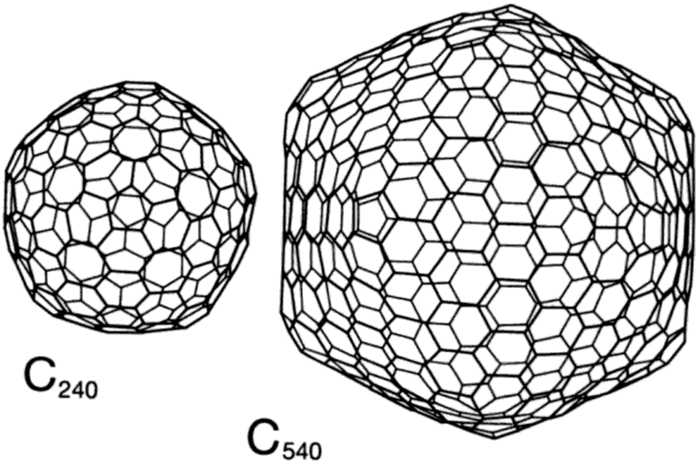


Figure 1.31 *Harry Kroto and his student Ken McKay found that highly symmetrical structures can be built for the giant fullerenes, such as C_{240} and C_{540}. Again they contain just twelve pentagons, which allow the cages to close. As the cages get bigger, the "corners," where the pentagons sit, get sharper. These giant fullerenes have not yet been isolated and purified in sufficient quantities to allow detailed structural studies, but it seems likely that they will exist in several isomeric forms.*

Figure 1.32 *Tubular fullerenes? These hollow carbon tubes, consisting of concentric graphite-like sheets, were discovered by Sumio Iijima in 1991. They are capped at the end by polyhedral or conical shells. The tubes, shown here in cross-section under the electron microscope, are typically one to fifty millionths of a millimeter in width. It is possible that the smallest tubes have hemispheres of* C_{60} *at the end. (Photograph courtesy of Sumio Iijima, NEC Corporation, Tsukuba.)*

isomers of the larger fullerenes to a manageable level. C_{70} has just two, it seems, and C_{78} perhaps eight or so (Figure 1.30). The giant fullerenes C_{120}, C_{240} and C_{540} are expected to have some particularly symmetrical isomers (Figure 1.31) but these molecules haven't yet been isolated in sufficient quantities to put this to the test.

Larger still are the fullerene-related structures discovered in 1991 by Sumio Iijima at the NEC Corporation in Tsukuba, Japan. He found that under certain conditions, the electrical-arc method of fullerene formation produces instead fine carbon fibers growing on one of the electrodes. Examination of these fibers under the microscope showed that they are hollow tubes comprised of graphite-like sheets curled into cylinders (Figure 1.32). Each tube contains several cylinders nested inside each other like Russian dolls. The tubes are capped at the end by cones or faceted hemispheres, which presumably contain pentagonal rings to allow the sheets to curl up. These graphite-like tubes, some just a nanometer in diameter (close to that of C_{60}) and up to a thousand times as long, are predicted to have some interesting properties. They should be the strongest carbon fibers known, and may also conduct electricity. At the end of 1992 Iijima and his colleague Pulickel Ajayan succeeded in breaking open the caps at the tube ends, whereupon the tubes sucked up liquid lead as if they were drinking straws. These carbon "nanotubes," and the related hollow, concentric carbon particles that have also been created in the carbon-arc method (Figure 1.33), are now developing into an entire subdiscipline of fullerene research.

It is now clear that graphite-like sheets provide an almost limitless capacity for forming carbon structures – the sheets can be curled up and folded like paper. This field of research has exploded so rapidly since the breakthrough of fullerene mass production in 1990 that it is virtually impossible to predict what tomorrow might bring. Richard Smalley has suggested, however, that of one thing we can be certain: "Buckminster Fuller would have loved it."

tives and the constituents of cosmetics, which generally bear little resemblance to the substances that went into their making. To many people, the very word "chemicals" denotes these highly synthetic substances ("this food contains too many chemicals"), as if to suggest that all chemicals are man-made. But the growing desire for a return to the use of natural products is not so much a flight from chemistry *per se* as a tacit acknowledgement that perhaps the chemistry of our own bodies is better attuned to that of nature, whose synthetic prowess (Berthelot notwithstanding) far exceeds our own.

The problem facing both the chemical industries and nature herself is how to rearrange often crude, simple starting materials into more useful compounds. This is generally much more than a matter of selecting starting materials that contain all the right atoms and mixing them up in a big pot – that is most likely to lead to a mixture of all manner of useless substances, amongst which that one desired may appear in tiny yields. Or perhaps nothing will happen at all – one will be left with a pot of well-stirred reagents, like an unbaked cake mix. What is needed for systematic chemical syntheses is a set of rules that will identify the likely outcome of a chemical process – what will be the major products, and under what conditions will the reaction occur?

It is relatively rare to find a useful chemical reaction that will proceed simply by adding together the reagents. But heat alone, or even just stirring or shaking, is sometimes sufficient to get things going. Light and electricity will do the job in other cases. Yet there are many important industrial processes for which these things are not enough, but for which a rather more mysterious agent of transformation is used: a substance that is not itself a reagent (since it is not consumed in the process) but which nevertheless initiates the reaction, which would not take place in its absence.

Substances of this sort, called catalysts, seem to have an almost magical ability: without becoming altered by losing or gaining atoms, they somehow enable a reaction to proceed. Some catalysts are particles of a bulk solid such as a metal or a metal oxide: others are single molecules that share a solvent with the reagents. Some are there just to initiate a reaction, but often they also determine the mixture of products obtained. In the United States, about 43 per cent of the total production of the chemical industries relies on the action of catalysts. The role of catalysts in the chemistry of living organisms, meanwhile, cannot be overemphasized. Scarcely a reaction in the body would be possible if it were not for the gentle assistance of nature's own catalysts, called enzymes.

While they may be in many ways the alchemical *lapis philosophorum* of modern chemistry, there is nothing mystical about the way that catalysts work. This chapter explains how a catalyst does its job, and provides a few illustrations of the exquisite control of chemical reactions that they can afford. It is important to appreciate, however, that catalysts cannot work miracles. They can help a reaction to occur, but only if the reaction is "feasible" in the first place. This is to say that we must make a distinction between whether a reaction *can* occur in principle and whether it *will* in practice. Catalysis can influence only the latter. To understand how it does so, we need first to see what it is that determines the feasibility of a reaction. Given a set of starting materials and a desired outcome in which they have combined into some useful substance, how can we know whether the transformation is possible?

The driving force of chemistry

The end product

Many chemical reactions appear to be strictly one-way processes. We begin with a set of compounds (the reactants) which, when mixed together under suitable conditions, undergo a transformation involving the rearrangement of atoms to yield a new set of compounds (the products). Chemists represent this process of reaction in a simple, schematic form according to which an arrow shows the transformation of reactants on the left-hand side to products on the right:

reactants → products

In many cases it is necessary, as noted already, to supply some encouragement to get the reaction going, perhaps by shaking the reactants together or by heating them. (In either case, what we are really doing is supplying energy.) But once the reaction has taken place, there appears to be no going back. The products can be left standing together for as long as we like without ever showing an inclination to rearrange their constituents back into the reactants. Consider, for example, burning a lump of wood in air. The reaction here is between the rather complex organic molecules in the wood fibers, mainly the carbohydrate called cellulose, and the oxygen molecules in air. The products will be chiefly carbon dioxide gas and water, along with nitrogen oxides from the nitrogen-containing molecules in the wood, and also a fair quantity of pure carbon in the form of soot and charcoal. The reaction has to be triggered by igniting the wood, but once underway it should continue of its own accord. Yet even if we carry out the burning in a closed box (containing sufficient oxygen) so that none of the products escapes, we will never at a later date open the box to find that the oxide gases and soot have miraculously recombined into the original block of wood and oxygen gas. In other words, the reaction

wood + oxygen → carbon and nitrogen oxides + water + soot

is feasible enough, but the reverse process is not.

The irreversibility of this example may come as no surprise: it is hard to conceive of the various oxide gases suddenly rearranging themselves into the complicated molecular structure of cellulose. There are plenty of simple reactions, however, for which the preferred direction is not obvious at all. Will a piece of zinc metal react with a solution of sulfuric acid into which it is dipped? Yes – but a piece of silver will not. Why, by the same token, does iron corrode in air to form the red iron hydroxide that we know as rust, while gold retains its pristine luster? Why does hydrogen gas combine explosively with oxygen gas to form water, rather than water explode into its constituents hydrogen and oxygen? The world is full of such mysteries.

That these are not *really* mysteries any longer is due to the efforts of the nineteenth century scientists such as the American Willard Gibbs, the Englishman James Prescott

Joule and the German physicist and physiologist Hermann von Helmholtz, whose work helped to establish the rules governing the direction of transformations in the natural world. Their studies were directed not primarily at chemical matters, however, but towards the rather more general question of how heat is transferred within and between different systems – a discipline known as thermodynamics (literally, the motion of heat). Thermodynamics is the fundamental science of transformations: it provides a scientific framework to describe all processes of change in the world, from the formation of black holes to the metabolic pathways of the body, from the way in which weather patterns are dictated by the supply of heat from the Sun to the consequences of an expanding Universe. Common to all these phenomena is the question: why do they proceed in the manner and direction that they do, and not in some other? Why does a drop of ink in water always disperse, but the uniformly tinted solution never unmix to reform the original droplet? Why doesn't water ever run uphill? Why, indeed, does time itself appear to flow only in one direction? Clearly, thermodynamicists have found themselves in the position of having to explain some very profound questions.

There is, however, a universal answer, which is embodied in the so-called Second Law of thermodynamics. (What, you might ask, is the First Law? It is that principle which is commonly known as the "conservation of energy" – energy is never destroyed, but only transformed from one kind to another.) The Second Law states that all realizable transformations are accompanied by an increase in the total amount of *entropy* in the Universe. (Strictly speaking, it says that the entropy cannot decrease; there is a class of transformations – those that can be reversed exactly – for which the entropy content of the Universe can remain unchanged.)

These days, entropy is a term not uncommon in everyday parlance, but it has acquired a certain air of mystery. There is, however, nothing very mysterious about it at all. It can be regarded as a measure of disorder – a pile of bricks, for instance, has more entropy than a house. Similarly, a liquid has a greater entropy than a crystal, since the former the molecules tumble about in disarray while in the latter they are stacked in an orderly, regular pattern. The Second Law is therefore saying that the Universe is bound to become ever more disorderly. This too can appear to be a very recondite and mysterious statement, but in fact it is saying nothing more than that things tend to happen in the most probable way: there is simply a greater probability that things will become disordered than the reverse. The Second Law is therefore actually a statistical law, which does not prohibit absolutely the possibility of a change that induces an decrease in entropy, but says only that such a change is overwhelmingly unlikely when we are considering huge numbers of molecules.

Uphill or downhill?

Although the Second Law of thermodynamics provides a universal arrow for specifying the direction in which change, chemical or otherwise, will occur, it is not actually of very much practical use to chemists. The problem is that the Second Law considers only the entropy of the entire Universe, which, as you might imagine, is not an easy thing to measure. In order to predict which way a chemical reaction will go, we need to know not just how the entropy of the reactants differs from that of the products, but also how the heat given off (or consumed) changes the entropy of the surroundings. How heat produced in a reaction changes the surroundings is hard to establish in detail – it will depend on the nature of the surroundings themselves. But fortunately we do not need to worry about these details – the entropic effect of heat dished out to the surroundings depends just on *how much* of this heat there is. If the loss or gain of heat by the chemical system is accompanied by a change in volume (if a gas is given off, for example), this also has an effect on the entropy of the surroundings. When there is a volume change of this sort, the chemical system is said to do work on the surroundings (this work can be harnessed, for example, by allowing the change in volume to drive a piston), and this work must also be taken into account in determining the total entropy change.

We can therefore determine the direction of a chemical change as specified by the Second Law on the basis of just the change in entropy of the reactants, the amount of heat consumed or evolved, and the work done on the surroundings. All of these can in principle be measured. Willard Gibbs expressed the directionality criterion in terms of a quantity called the Gibbs free energy, which quantifies the net effect of these various contributions on the total change in entropy during the transformation. The Gibbs free energy represents the balance between the change in entropy of the system and the change in entropy of the surroundings; the latter is represented by a quantity called the enthalpy, which is the sum of the heat change (due largely to the making and breaking of chemical bonds) and the work done (due to a change in volume).

A chemical reaction is feasible if there is an overall increase in entropy of the system and its surroundings (the latter being an effective representation of the rest of the Universe); this means that, for example, if the products have less entropy than the reactants, this decrease must be more than balanced by an increase in entropy of the surroundings due to the heat given out or the work done via volume changes. This translates into the rule that the Gibbs free energy must decrease. (Strictly speaking, this is true only when the temperature and pressure of the system are held constant. Under different conditions, other kinds of free energy must be considered instead of that defined by Gibbs.) The change in Gibbs free energy therefore defines the "downhill" direction for the reaction. In the same way that a ball perched atop a hill will run down it, thereby reducing its potential energy (the value of which depends on the ball's height above the ground), a chemical reaction will tend to proceed in that direction in which it loses free energy (Figure 2.1).

The kinetic hurdle

The possible and the actual

The "decreasing-free-energy" criterion seems to suggest that neither this book nor you the reader should exist. That is to say, free energy would be decreased significantly if

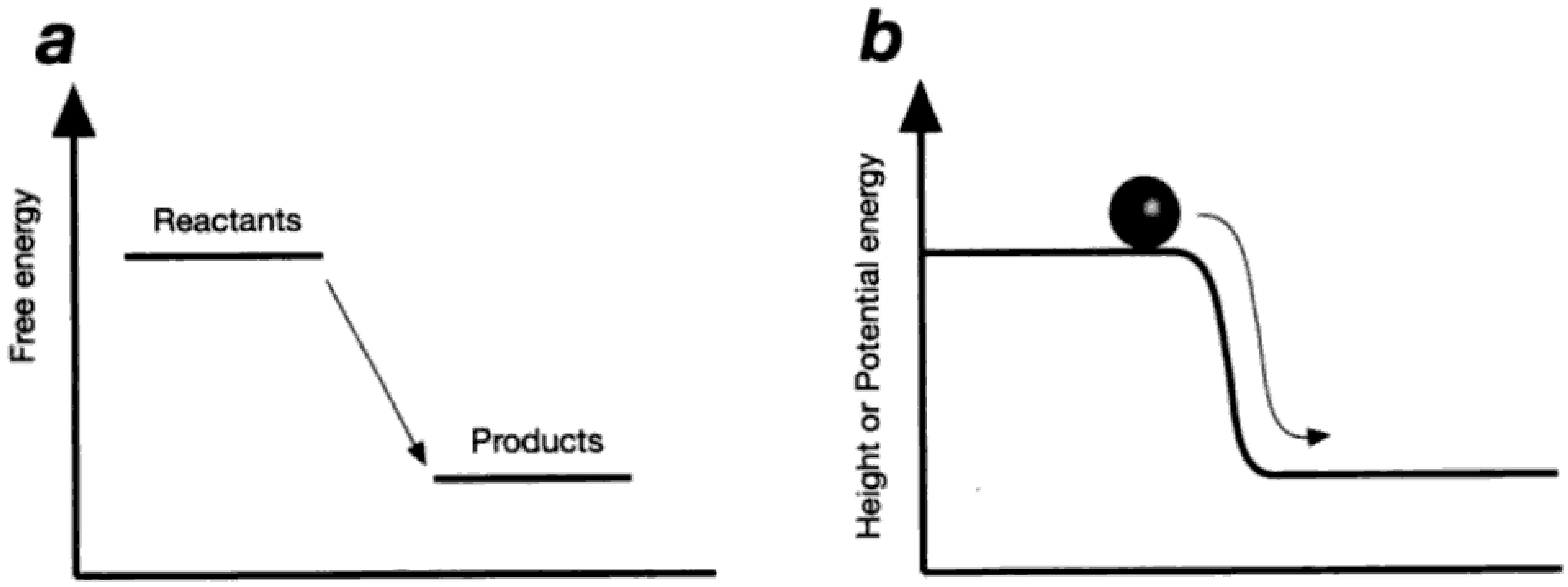


Figure 2.1 *The "downhill' direction of a chemical reaction is determined (under conditions in which the temperature and pressure are held constant) by the Gibbs free energy: the reaction can proceed in that direction for which the Gibbs free energy of the end products is less than that of the starting materials (a). Similarly, a ball can lower its potential energy spontaneously by rolling down a hill to a lower level (b); but it will not spontaneously roll uphill.*

both were to burst into flames. Indeed, not only does combustion of organic matter give out a lot of heat, increasing the entropy of the surroundings, but converting the orderly molecular structures in our bodies or in the fibers of paper into disorderly molecules of gaseous carbon dioxide and water is accompanied by a vast increase in entropy of the products. So all is geared towards a considerable boost for the total entropy of the Universe, which is to say, a large decrease in Gibbs free energy. Yet unless the book or (heaven forbid) the reader is thrown onto a bonfire, both will continue to exist in our oxygen-rich atmosphere for a considerable time to come. So what is wrong with Gibbs's criterion for determining whether a chemical transformation is up- or downhill?

Happily, there is nothing wrong with it. But it is a criterion for deciding only whether the reaction is feasible *in principle* (which it clearly is). It says nothing about what will happen *in practice*. The vast majority of chemical reactions that are downhill processes turn out to be hindered by a barrier that prevents them from occurring, at least at any significant rate. What determines the feasibility of the reaction is the thermodynamics – considerations of enthalpy, entropy and free energy. But what hinders the reaction from proceeding is the so-called "kinetics" of the transformation.

To understand kinetic hindrance, we need to consider what is happening during a reaction at the molecular level. The way in which atoms are linked together in the product molecules is invariably different from their arrangement in the reactants; this is the very essence of chemical change. The transformation therefore requires that bonds be broken and/or formed. Regardless of what the relative intrinsic energies of the reactant and product molecules might be, the breaking of bonds requires energy. In other words, the initial step of a reaction is generally an uphill process: energy must be supplied to snap the molecules apart before their atoms can recombine (with a concomitant release of energy) into new configurations. Even if a reaction can potentially release a large quantity of free energy, it can proceed only if energy is first supplied in order to of both the forward and the backward reactions, and thus we hasten the progress towards thermodynamic equilibrium.

But heating is a rather crude way of increasing a reaction's rate, and may bring with it complications. For a start, it makes the reaction more expensive to carry out, as we have to supply it with energy. And one may find that either the reactants or the product are unstable at high temperatures – raising the temperature may accelerate other, undesirable processes such as the break-up of the very molecules that one wants to form. The proportion of molecules that have sufficient energy to overcome the barrier to reaction depends not only on the temperature, however, but also on the height of the barrier. If we could lower the barrier, more molecules would be able to react at a given temperature, and equilibrium will accordingly be reached faster.

The height of the barrier is determined by the free energy of the transition state, which is itself dependent on the molecular structure of this ephemeral entity. The function of a *catalyst* is to decrease the free energy of the transition state, thus making it a less unstable species. More precisely, the catalyst must interact with the reactants so as to form a modified transition state at a lower cost in free energy (Figure 2.4). A true catalyst must emerge from this interaction unscathed: once over the free energy hill, the transition state must evolve into the products without permanently changing the state of the catalyst, leaving it free to do its job again on other reactant molecules. If the catalyst were somehow altered or consumed in the process, we would have to renew it constantly; indeed, it would then not really be a catalyst at all, but merely another reactant.

Broadly speaking, catalysts come in two classes. To illustrate the difference between the two, imagine the reactant molecules as a timid couple who, despite being made for each other, would be too shy ever to unite as a pair if left to their own devices. The first way to catalyze the union is to add into the equation a matchmaker who will bring the two together, introduce them and kick off the date by starting a conversation to which they can both contribute. In chemical terms, the catalytic matchmaker is a single

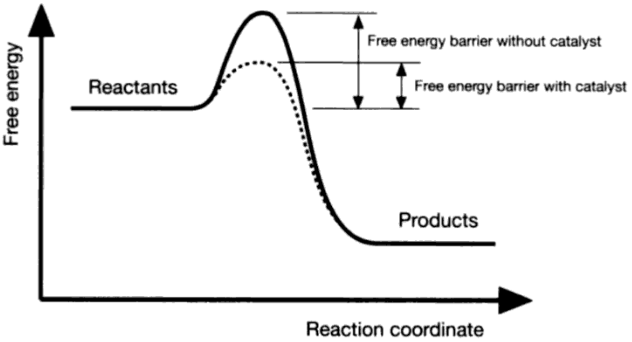


Figure 2.4 *The function of a catalyst is to lower the free energy barrier to reaction; in other words, to lower the free energy of the transition state.*

molecule, just like the reactants, and will be in the same physical state as the reactants – all, for example, may be in the gas phase or in solution. This type of catalysis is said to be homogeneous.

Alternatively we could arrange for our pair to meet in an environment conducive to their becoming relaxed and friendly; as they are, let us say, both music lovers, we arrange for them a night at the opera, in which situation the relationship should flourish. Catalysts that provide favorable environments for the reaction generally have to be in a different state to the reactants – they are usually solids, while the reactants are liquids, gases or solutes. The environment in which the reactants get together is often the surface of the catalyst, on which the chance of a reaction is enhanced; other catalysts in this class contain molecular-scale cages or tunnels in which the reactants are trapped and held together in intimate proximity. This type of catalysis is called heterogeneous. Some researchers are now turning their attention to catalysts that lie at the boundary between homogeneous and heterogeneous systems: clusters of atoms that are bigger than the reactant molecules, but only a little. It is hoped that this new field of catalysis, still very much in its infancy, might combine some of the advantages of both approaches.

Homogeneous catalysts are generally molecules that have been carefully selected or designed to interact with the reactants in a very specific way, often to ensure that just one of several possible products is formed. The successful design of such catalysts requires a detailed knowledge of the way in which the reactants interact both with each other and with the catalyst, and it is only in recent decades that this sort of information has been easily accessible; in earlier times, homogeneous catalysis was very much a case of trial and error. Homogeneous catalysts are potentially capable of more delicate tasks than most heterogeneous varieties, and there is no better illustration of this delicacy than that provided by enzymes – homogeneous catalysts designed by nature. Although enzyme catalysis is still understood only in a rudimentary fashion, it is clear that it has much to teach us about designing synthetic homogeneous catalysts.

Heterogeneous catalysis is an older, more traditional approach. While these catalysts are commonly cruder and less selective than their homogeneous rivals, they have been and remain the mainstay of much of industrial chemistry, and sometimes play an important role in natural processes too. In recent years, moreover, new heterogeneous catalysts have been developed which demonstrate a degree of selectivity to rival that of homogeneous systems.

Staying on the surface

Metal surfaces are the archetypal heterogeneous catalysts, in particular those of the transition metals such as nickel, palladium and platinum. These materials are able to induce a wide range of reactions between gases that would otherwise hardly proceed at all (Table 2.1). In the presence of platinum metal, carbon monoxide and oxygen combine to form carbon dioxide, a process central to the operation of catalytic

Table 2.1 Some important metal-catalyzed industrial reactions

Metal catalyst	Reaction
nickel	hydrogen + unsaturated vegetable oils → saturated vegetable oils
iron	nitrogen + hydrogen → ammonia
silver	ethylene + oxygen → ethylene oxide
platinum/rhodium	ammonia + oxygen → nitric acid
iridium/rhodium	carbon monoxide + oxygen → carbon dioxide

converters. Nickel can induce all kinds of unsaturated hydrocarbons to react with hydrogen to form saturated compounds. This is an important process in the food industry since it converts unsaturated vegetable oils to their saturated counterparts. Ammonia, a crucial component of fertilizers and explosives, is manufactured in vast quantities by the Haber process, the reaction of nitrogen and hydrogen over an iron catalyst. Nitric acid is produced from ammonia and oxygen, courtesy of a catalytic mixture of platinum and rhodium metals; the production of polyethylene from ethylene uses catalysts based on chromium and titanium; and the petrochemical industry, which manufactures from crude oil all manner of hydrocarbon compounds for plastics, fuels and other uses, relies heavily on platinum and other metal catalysts.

In all of these examples, reactions that are hindered by often formidable free energy barriers are greatly accelerated in the presence of the metal surface. The general principles of the catalytic mechanism are the same in every case, relying on the anomalous reactivity of metal atoms at the surface of the material. These exposed atoms have a strong capacity for forming bonds, and will readily bind gas molecules that impinge on the surface – a process known as adsorption.

The strength of the interactions between the surface atoms of the metal and the adsorbed gas molecules (called the adsorbate) can vary considerably, depending on the chemical nature of the two. Sometimes full-blown chemical bonds are formed, and the gas molecule is therefore held in place quite tightly and rigidly. This is called chemisorption, short for "chemical adsorption." Alternatively the bond can be a fairly weak one, strong enough to hold the adsorbate close to the surface but not, perhaps, to prevent it from wandering from one surface atom to the next. This is physisorption ("physical adsorption").

When it undergoes adsorption onto a surface, a gas molecule cannot remain unmoved by the experience. A chemisorbed molecule can form a new bond only by rearranging its existing bonds; and even for physisorption a new bond of sorts is formed, necessarily weakening those within the adsorbed molecule. When ethylene becomes attached to platinum, for example, the double bond between the two carbon atoms is broken open and both carbon atoms form bonds to platinum (Figure 2.5*a*). The weakening of bonds in the adsorbate is often so pronounced that the molecule falls apart, leaving atoms or molecular fragments to wander over the surface. On iron, for example, carbon

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