Chapter 1
Ode to the Chemical Element Carbon

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Abstract If an element deserves praise, then this element is carbon. Its nucleus, along with N and O, catalyzes the fusion of H into He in the sun and sun-like stars. Its minor stable isotope allows chemical structure to be elucidated by^{13}C-NMR, along with^{1}H-NMR. Its long-lived radioisotope ^{14}C allows radiocarbon dating, and reaction mechanisms or bioactivities of medicines to be understood by isotopic labeling. Its short-lived radioisotope ^{11}C is used for PET scans. The 16th part of its atomic weight serves as *unified atomic mass unit*, also called "dalton". Its allotropes (diamond, graphite, fullerenes) have extremely useful properties. And this above all: it is the element that life is based upon, the central element of organic chemistry, and the element that is present in most of the 7×10^7 substances registered till now. Due to this fact and to the multiple uses of carbon compounds, although it is now known that they do not differ from inorganic compounds, Organic Chemistry is still a distinct part of chemistry. Because carbon atoms form molecules with covalent bonds that can be represented by hydrogen-depleted molecular graphs, this makes molecular structure search the best scientific documentation among all sciences. Substantial consideration is dedicated to carbon allotropes and to derived hydrocarbon fragments such as diamondoids and benzenoids, emphasizing the author's theoretical contributions to these research fields.

1.1 Isotopic Carbon Nuclei

Six protons need six or seven neutrons in order for the nuclear strong force to hold together all these nucleons for a longer time than about 10^{15} years (resulting in what are called 'stable nuclides'). "Stable" is a relative notion, connected with our ability of detecting radioactive decays; probably in the future when this ability will increase, deuterium and other nuclides may be found to be very weakly radioactive, having very long half-lives, longer than those of the naturally-occurring primordial nuclides^{232}Th,^{233}U,^{235}U,^{238}U. With only five neutrons, the ^{11}C nucleus is a positron-emitter with a half-life of 20.4 min; with eight neutrons, the ^{14}C nucleus is an

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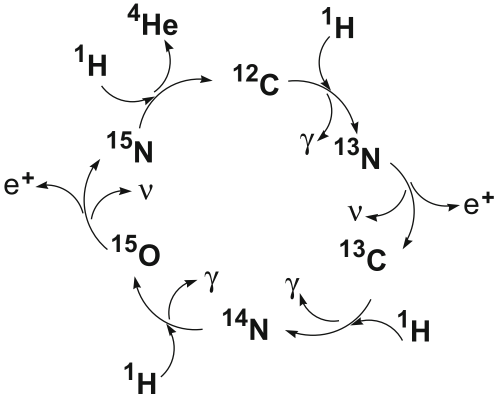


Fig. 1.1 The fusion of four protons (^{1}H) affording a ^{4}He nucleus (α-particle)

electron-emitter with a half-life of 5730 years. We will examine briefly each of these four carbon nuclides.

First, starting with the stable^{12}C, which accounts for 89.9 % of all carbon atoms, it is formed in the interior of stars by the triple-alpha process. It is no longer a mystery how three α-particles interact in the nucleus despite the electrostatic repulsion (two α-particles cannot form a stable^{8}Be nuclide): it was recently calculated that in the ground state of the ^{12}C nucleus, three α-particles form a triangle cluster, whereas with low-energy excitation they form a kinked obtuse-angle cluster (so-called Hoyle state) shaped like a bent arm (Epelbaum et al. 2011; Lee et al. 2012). Pairing of nuclear spins for protons and neutrons in even-even nuclei such as ^{2}He,^{12}C,^{16}O results in such nuclei to be devoid of magnetic moments.

In the sun and other sun-like stars, fusion of hydrogen nuclei to helium involves a process discovered by Hans Bethe, who was honored for it in 1967 with the Nobel Prize for Physics. A catalytic cycle involving ^{12}C,^{13}C,^{13}N,^{14}N,^{15}N, and ^{15}O nuclei allows this fundamental process to occur; 2 positrons, 2 neutrinos, and 3 gamma photons carrying away the fusion energy are also released (Fig. 1.1). In the Bethe cycle there are four stable nuclides (^{12}C,^{13}C,^{14}N,^{15}N) and two positron + neutrino-emitters:^{13}N ($T_{½} = 10$ min) and^{15}O ($T_{½} = 2$ min). Positrons undergo rapid annihilation on encountering electrons, further increasing the emitted fusion energy during the life-time of the star.

An important characteristic of the ^{12}C and ^{13}C nuclei is their small cross-section for neutron capture. Thus, despite their higher mass than that of deuterons or protons, which could thermalize better the fast neutrons released during the fission of ^{235}U, the first nuclear reactor was built by E. Fermi and coworkers in Chicago by using pure graphite as moderator. This use of graphite has several drawbacks: (i) small amounts of impurities reduce substantially its efficiency, and this is why Hitler's Germany opted for using heavy water as moderator in the 1940s; (ii) nuclear radiations cause lattice defects ("E. P. Wigner defects") which may release large amounts of energy, as it happened in 1957 in the Windscale reactor fire in UK; (iii) at higher temperature it can burn, as it happened in the Chernobyl disaster, Ukrainian Soviet Republic in 1986.

Second, the ^{13}C nucleus accompanying ^{12}C as a minor constituent (about 1 % of all carbon atoms) has a magnetic moment, and as such allows nuclear magnetic resonance of carbon atoms in organic compounds.

Third, for archaeology the existence of the long-lived beta-emitter^{14}C has been a blessing, allowing radiocarbon dating of any old organic finds between a few 100 years and about 60,000 years. Willard Libby was awarded the 1960 Nobel Prize in chemistry for this work. All living organisms assimilate during their lifetime a small amount of radiocarbon because high-energy neutrons from cosmic rays convert continuously a small amount of ^{14}N nuclei into ^{14}C nuclei via the following nuclear reaction, in which a proton is released:

$$^{1}_{0}n + ^{14}_{7}N \longrightarrow ^{1}_{1}H + ^{14}_{6}C$$

The resulting carbon atoms are immediately oxidized to CO_2 that mixes in the earth's atmosphere; then photo-assimilation and metabolic reactions cause an equilibrium concentration of radiocarbon in all organic constituents. As long as the plants or animals are alive, the amount of radiocarbon remains constant, but after their death the radioactivity decays exponentially according to the well-known first-order kinetics. Tree rings allow the calibration of radioactive dating, and one can see the spike due to atmospheric nuclear bomb tests in the 1960s. Libby demonstrated the accuracy of radiocarbon dating by estimating the age of wood for which the age was known, including an ancient Egyptian barge of 1850 before the Christian era.

Fourth, compounds labeled with positron-emitting nuclei such as ^{11}C,^{13}N,^{15}O and ^{18}F are used for positron emission tomography; [^{11}C]glucose or [^{18}F]fluorodeoxyglucose can detect metastasis spreading of cancer cells; other ^{11}C-labeled compounds may be used to diagnose Alzheimer disease or leukemia. The short half-life ensures the rapid disappearance of radioactivity but requires a facility for producing the radionuclide and incorporating the label in the proximity of the medical facility. Positrons are immediately converted into easily-detected gamma-rays by annihilation with electrons.

1.2 Carbon Atoms

Mendeleev's crucial discovery of the Periodic System was based on atomic weights of the elements known at that time, and on his intuition that a deeper principle must govern this *system* (this is why he used this word, instead of today's term "periodic *table*"). He dared to "stick out his neck" by inverting the order between I and Te (and later between Ar and K) and also by predicting properties of three new elements, Sc, Ga, Ge. Mendeleev was fortunate to see them discovered during his lifetime. Despite many nominations, the Nobel Foundation never honored him.

The first atomic mass unit (*amu*) was taken by J. Dalton to be the mass of a hydrogen atom (1803). Binary hydrides are, however, less common than binary oxides, so that oxygen was more convenient and the *amu* was defined as the 16th part of the atomic mass of oxygen. Refined methods were used for exact measurements of atomic weights, correcting some erroneous data that had been confusing in Mendeleev's time. T. W. Richards was awarded the 1914 Chemistry Nobel Prize (distributed in 1915) for his work on atomic mass determinations. However, after 1912 when the newly invented mass spectrometer revealed the existence of ^{17}O and ^{18}O stable isotopes along with the predominating ^{16}O (99.66 %), physicists based their determinations on the atomic weight of ^{16}O, whereas chemists continued to use the old definition of *amu*, involving the weighted average of all three stable oxygen isotopes; thus chemists had a unit which was more massive by 1.00028 than the physicists' unit. It was only in 1961 that IUPAC, IUPAP, and IUB agreed on redefining the "unified atomic mass unit" as the 12th part of the mass of a ^{12}C atom. After the SI unit "kg" was redefined in 2012, the present-day definition of atomic weights remains based on carbon atoms and Avogadro's number (N_A) as 1 dalton (Da) $= 0.001/N_A$ (in kg) (Holden 2004). However, there is an ongoing discussion on the compatibility between the three related SI units (mole, kilogram, and dalton) after fixing the Planck constant and Avogadro's constant (Leonard 2012).

After discussing the role of carbon in the thermonuclear cosmic formation of helium from hydrogen, it is not surprising that carbon is the *4th most abundant element in the universe by mass*, after $_1$H, $_2$He, and $_8$O. One should not forget that 2 and 8 are magic numbers of nucleons (protons and neutrons), so that $^4_2$He, $^{16}_8$O are double-magic nuclei.

Carbon is the *15th most abundant element in the Earth's crust*, and it is the *2nd most abundant element by mass in the human body* (18.5 %) after oxygen (65 %); it is followed by hydrogen (10 %) and nitrogen (3 %).

The most important chemical reaction occurring naturally on this planet is the photo-assimilation of carbon dioxide. In this reaction (catalyzed by chlorophyll in plants and algae, or by phycocyanin in cyanobacteria) the energy of sun's photons is driving the conversion of carbon dioxide and water vapor into glucose and oxygen.

$$6CO_2 + 6H_2O + \text{energy} \longrightarrow C_6H_{12}O_6 + O_2$$

All the oxygen in our atmosphere originates in this reaction, and the energy released in the reverse reaction allows animals feeding on plants to proceed with their metabolism. Glucose and other simple raw materials such as phosphate, ammonia, and mineral salts are processed by living cells into all constituents of living cells: other carbohydrates, lipids, proteins, and polynucleotides.

Carbon dioxide from the atmosphere is replenished by the well-known *carbon cycle* with the participation of carbon sources from the geosphere, hydrosphere, biosphere, and pedosphere. The amount of carbon (in Tt, teratonnes, 10^{15} kg) in the major reservoirs is 0.7 for the atmosphere, 40 for the hydrosphere, and 75,000 for the geosphere (60,000 for the sedimentary carbonates and 15,000 for kerogens). Even carbon from the calcium/magnesium carbonate rocks is recycled via volcanic emissions triggered by plate tectonics. Throughout most of our planet's history, volcanoes provided the highest turnout of CO_2, but after the industrial revolution, human contribution by the increasing burning of non-renewable fossil fuels (all based on carbon, namely coal, natural gas, and petroleum) has outpaced volcanic emissions hundredfold. The estimated amount of carbon in accessible fossil fuels is about 5 Tt.

1.3 Carbon Chemical Bonding

Atomic orbitals 2s and 2p host the four valence electrons of carbon in the ground state configuration $1s^2 2s^2 2p^2$, but the covalent bonds have different energies and geometries (length and bond angle) according to the hybridization. Having an electronegativity situated midway between the extremes (fluorine and cesium), similarly to hydrogen, carbon is able to form stable long chains or rings with itself. Divalent sulfur also has this property, but this leads only to sulfur element allotropes. Alternating SiO bonds can also lead to long chains, and the resulting mineral silicates form a large part of the Earth's crust. However, only carbon's bonds were selected by the evolution of life on our planet. The huge diversity of carbon compounds makes this unique element the central constituent of the 7×10^7 substances indexed till now in the *Chemical Abstracts Registry* database, and this fact justifies the study of Organic Chemistry in a distinct class of chemical compounds. Indeed, more than 95 % of the 70 million substances are organic. Unlike the combinatorial large but finite number of inorganic substances (excluding silicates), the number of possible hydrocarbons is infinite. Along with carbon and hydrogen, most of the known organic substances contain only a small number of other elements: O, S, N, P, F, Cl, Br, I. The element carbon appears as a tetravalent anion only in few methides (Al_4C_3 and Be_2C) that produce methane with water or acids; other carbides contain C_2^{2-}or C_3^{4-} and afford acetylene or allene/propyne, respectively (Cotton et al. 1999). Silicon and boron form with carbon hard covalent tridimensional lattices. Although stable carbocations, free radicals, or carbenes exist when electronic delocalization is present, the overwhelming majority of carbon compounds form molecular covalent bonds.

Although it is impossible to enumerate all the uses and applications of organic compounds, one should mention that the marked increase of life expectancy during the last centuries is mainly due to the progress of medicinal chemistry and detergents; local and general anesthetics allow surgeons to perform operations and organ replacements that were unimaginable a century ago; nowadays plastics tend to become the preferred materials; dyestuffs and synthetic textiles surround us; Alfred Nobel's fortune was due to the invention of dynamite, an organic explosive; pesticides and herbicides contribute to increasing productivity of agriculture; organic compounds contribute to the electronic industry, liquid crystals for color screens, heat transfer agents for air conditioners and refrigerators, etc.

Living cells produce powerful catalysts, enzymes, which are proteins. In many cases biosynthetic reactions proceed on the basis of effects caused by carbonyl groups. The chemical reactions allowing chemists to synthesize new organic compounds involve, however, bonds with other types of atoms. As an illustration, the following paragraph contains a list of such atoms (in brackets) associated with the name of a chemist awarded Chemistry Nobel Prizes for the discovery of efficient synthetic procedures. The list is far from being exhaustive.

V. Grignard 1912 (Mg); K. Ziegler and G. Natta 1963 (Ti, Al); E. O. Fischer, G. Wilkinson 1973 (Fe, Cr); H. C. Brown 1979 (B, H); G. Wittig 1979 (P); R. F. Heck, A. Suzuki 2010 (Pd); E. Negishi 2010 (Zn, Pd); R. H. Grubbs, R. R. Schrock 2005 (Ru, Rh). A few other names follow that have not been honored by the Nobel Foundation, yet they have discovered important organic reactions involving various other heteroatoms: E. Frankland (Zn); H. Gilman (Cu); J. K. Stille (Sn).

1.4 Chemical Abstracts Service: Documentation in Chemistry versus Other Sciences

On the occasion of its centennial anniversary in 2007, Chemical Abstracts Service (CAS) issued a Special Issue of *Chemical & Engineering News* in which the CEO of CAS, Robert J. Massie, gave details of what CAS is and what it does (Massie 2007). CAS qualifies as a "national treasure". Moreover, by adopting a graph-theoretical approach to chemical structures represented as hydrogen-depleted molecular graphs that can be traced on a computer screen and then linked to the CAS database, it is possible to learn in a matter seconds if any covalent structure has ever been described in a publication or a patent. Thus chemistry, considered to be the Central Science (Brown et al. 2011; Balaban and Klein 2006) because it bridges the hard sciences such as mathematics, physics, or astronomy with the soft sciences such as biomedical, economic and social sciences, is nowadays also the best-documented science. One can never be certain if a mathematical theorem or a physical property has been described earlier, because these are expressed in words, and the association between words and the corresponding theorems, properties, or ideas is not unique. Of course, this limitation applies also to chemistry when it uses words and not structural formulas.

Before the "computer age", the IUPAC Nomenclature Committee had devised elaborate rules for naming chemical substances: the "Red Book" for inorganic substances, and the thicker "Blue Book" for organic substances. Yet despite spending hours or days in the library for looking into the Collective Molecular Formula Indices of *Chemisches Zentralblatt* (till 1945) or *Chemical Abstracts* (1907–1986), one could never be quite sure that one could access all documentation for a given substance because of the intricacy of chemical isomerism and nomenclature. All this uncertainly is now a problem of the past, as long as one can draw a constitutional formula as a hydrogen-depleted molecular graph, provided that one has access to SciFinder. An agreement between CAS and FIZ Karlsruhe gave rise to STN International, which is an online database service that provides global access to published research, journal literature, patents, structures, sequences, properties, and other data.

Table 1.1 Comparison between diamond and graphite

Property	Diamond	Graphite
Aspect	Transparent, highly refractive	Opaque, black
Crystalline system	Cubic	Hexagonal
Density (g × cm^{-3})	3.514	2.266
Hardness (Mohs scale)	10	Between 1 and 2
Electrical conductivity	Low	High
Thermal conductivity	High	Low

1.5 The Hard and Dense Carbon Allotrope, Diamond, and Its Diamondoid Hydrocarbon Relatives

We will discuss *infinite nets* whose peripheral bonds (usually connected to heteroatoms such as H or O) can be neglected, as well as *molecules*, all of whose atoms have to be taken into account. In the present survey the molecules to be discussed will be hydrocarbons, considered to be smaller fragments of the nets with hydrogen atoms connected to the peripheral dangling bonds. Whenever trillions of billions of molecules are identical we call them “substances”, otherwise we have mixtures. With two exceptions, natural or synthetic macromolecular polymers are mixtures with various degrees of dispersion. The narrower the dispersion, the closer is the polymer to a pure substance. The two exceptions (macromolecular compounds that are at the same time pure substances) are the natural polymers proteins and polynucleotides.

The hardest material on the Mohs scale is a carbon allotrope, diamond, formed in the earth’s interior at high temperatures and high pressures (HTHP), and brought to the surface by forces derived from tectonic plate movements. In 1946, P. W. Bridgman was awarded the Nobel Prize for Physics for his research on high-pressure devices. “Bridgman’s opposed anvils” were essential in General Electric’s HTHP method that used graphite and nickel at pressures of 5.4 GPa (54 kbar) and temperatures around 1720 K. At normal temperatures and pressures, graphite is thermodynamically more stable than diamond by about 0.2 kcal/mol, but the interconversion kinetics has a huge activation barrier so that “diamonds are forever”. Table 1.1 illustrates a comparison between the two common carbon allotropes.

In diamond (Fig. 1.2) all carbon atoms have sp^3 hybridization, all CC bonds have bond distances of 1.54 Å and bond angles of 109.5°. The conformation of CC bonds is staggered, minimizing the electrostatic repulsions, so that one can distinguish adamantane cells in the cubic lattice, which is identical to the zinc sulfide sphalerite lattice.

A different carbon allotropic hexagonal lattice is present in lonsdaleite, which contains iceane units having eclipsed CC bonds with Pitzer strain and a hexagonal (wurtzite) lattice. Figure 1.3 presents hydrogen-depleted formulas of adamantane ($C_{10}H_{16}$) and iceane ($C_{12}H_{18}$).

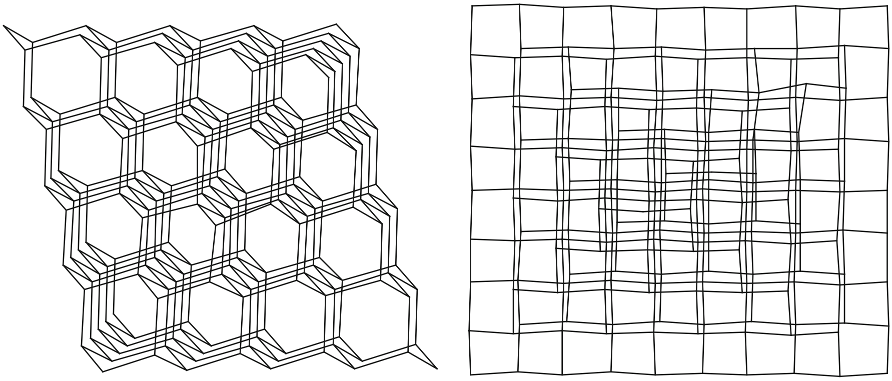
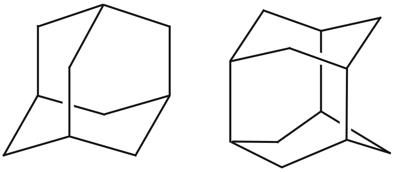


Fig. 1.2 A portion of the diamond lattice seen sideways (*left*) and up-front (*right*)

Fig. 1.3 Hydrogen-depleted formulas of adamantane (on the *left*) and iceane (on the *right*)



Recently, two exoplanets supposed to have huge amounts of diamond layers have been discovered when astronomers observed them transiting across their host star. The first one gravitates around a millisecond pulsar at a distance of 4,000 light years from us, and has a radius about ten times larger than that of earth, whereas the second one is at a distance of only 40 light years, has a radius twice larger than that of earth, and circles around 55 Cancri. Mass and radius estimates of this “55 Cancri e” planet suggested that it has a molten iron core surrounded by successive layers of silicon carbide, silicates, graphite and diamond (Madhusudhan et al. 2012).

The diamond lattice may be expanded theoretically by replacing each $C-C$ bond by the sequence $C-C\equiv C-C$, affording thereby “polyyne-diamond” (Melnichenko 1982; Kijima 2005); this replacement may be carried out in one, two, or three dimensions, and combines sp^3 with sp hybridization. It was emphasized by Kroto that a one-dimensional carbon allotrope with sp hybridization (carbyne) has no chance of existence as a stable substance (Kroto 2010).

Other theoretical possibilities of carbon nets, combining this time sp^3 and sp^2 hybridizations, were calculated more than 40 years ago (Balaban et al. 1968) and continued in later years; the topic has been reviewed by the present author in book chapters (Balaban 1989, 1998, 2013a). He collaborated with Roald Hoffmann and K. M. Merz in order to predict the stability of infinite nets having ordered arrangements of sp^3 and sp^2 hybridized carbon atoms (Merz et al. 1987). Interconversions between diamond and graphite must start with local hybridization changes, which were investigated theoretically (Balaban and Klein 1997). The near coincidence between certain interatomic distances in the diamond and graphite nets allowed some calculations of diamond-graphite hybrids (Balaban et al. 1994).

In books edited by Diudea (Diudea 2005; Diudea and Nagy 2013) one may read about some other possible types of diamond nets. It is stimulating to look at an ornamental diamond jewel with dimensions d measured in millimeters, and to think that one can look at this single *macromolecule* in which the carbon atoms constitute most of the atoms (their number is proportional to d^3), whereas any peripheral atoms such as H are much less numerous (their number is proportional to d^2).

The history of diamond hydrocarbons (or diamondoids for short) starts in 1933 with Landa's discovery of adamantane in petroleum (Landa and Mahacek 1933), confirmed a few years later by its elaborate synthesis (Prelog and Seiwerth 1941). The story might have ended there but for two fortuitous events. The first was Schleyer's serendipitous finding that $AlCl_3$ catalyzes the isomerization of the hydrogenated cyclopentadiene dimer into adamantane (Schleyer 1957, 1990). This discovery was made possible by adamantane's incredible volatility, paradoxically associated with a high melting point (actually adamantane sublimes around 270° without melting) (Mansoori et al. 2012). Soon afterwards Schleyer and his coworkers succeeded in synthesizing diamantane and triamantane using similar isomerizations (Cupas et al. 1965; Williams et al. 1966; Fort and Schleyer 1964; Fort 1976). The driving force in these reactions is increased thermodynamic stability: diamondoids are the perfect hydrocarbons for sp^3 hybridization. Unfortunately, the labyrinth of 1, 2-rearrangements becomes too complicated and only one tetramantane isomer could be obtained synthetically (Burns et al. 1976; McKervey 1980).

The IUPAC name of diamondoid hydrocarbons ([n]polymantanes) based on von Baeyer's conventions for polycyclic hydrocarbons becomes extremely awkward as the number n of adamantane units increases, as will be seen in the next paragraph. One must also take into account that starting with $n = 4$ more than one isomer is possible, so that one needs a shorter and simpler name, as well as a coding system and an understanding on how the carbon atoms are partitioned among quaternary, tertiary, and secondary groups. This was achieved by means of dualists (inner dual graphs) whose vertices are the centers of adamantane units and whose edges connect adjacent vertices corresponding to adamantane units sharing a cyclohexane ring. The code is simply a sequence if digits 1, 2, 3, or 4 representing the four tetrahedral directions around a carbon atoms according to simple conventions of minimizing the number in that sequence (Balaban and Schleyer 1978). Dualists are a special kind of graphs, in which the angles between edges do matter. For specifying substituent positions, however, IUPAC names have to be used; a general procedure to find IUPAC names exists for zigzag catamantanes (Balaban and Rücker 2013).

Adamantane is tricyclo[$3.3.1.1^{3,7}$]decane; it has molecular formula $C_{10}H_{16}$ and partitioned formula $(CH)_4(CH_2)_6$. Diamantane is pentacyclo[$7.3.1.1^{4,12}.0^{2,7}.0^{6,11}$]tetradecane and has code [1]; it has molecular formula $C_{14}H_{22}$ and partitioned formula $(CH)_6(CH_2)_8$. Triamantane is heptacyclo[$7.7.1.1^{3,15}.0^{1,12}.0^{2,7}.0^{4,13}.0^{5,11}$]octadecane and has code [12]; it has molecular formula $C_{18}H_{26}$ and partitioned formula $C(CH)_8(CH_2)_9$. These diamondoids are unique isomers (Fig. 1.4), but starting with $n = 4$, more than one isomeric [n]polymantane are possible.

By means of dualists it was possible to classify polymantanes into *catamantanes* when their dualists are acyclic, perimantanes when they have dualists containing

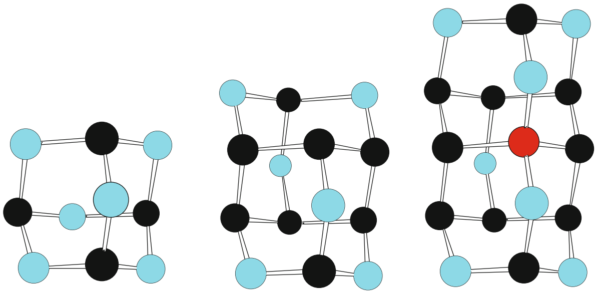


Fig. 1.4 Adamantane, diamantane, and triamantane; *red*, *black*, and *blue* denote *quaternary*, *tertiary*, and *secondary* carbon atoms

6-membered rings, and coronamantanes when they have dualists with larger rings that are not peripheries of condensed 6-membered rings. The dualist of a catamantane mimics the carbon skeleton of a staggered alkane. In turn, [*n*]catamantanes can be regular when their molecular formula is $C_{4n+6}H_{4n+12}$, or irregular when they have lower numbers of C and H atoms for a given *n* value. Codes of irregular catamantanes have one or more repeated digits *a* in a code sequence . . . *abca*. . . So far, all possible [*n*]polymantanes with $n < 8$ have been theoretically discussed. Some of them, like [123]tetramantane, are chiral, and exist as two distinct stable stereoisomers (Fig. 1.5).

The second fortuitous event was the discovery of large amounts of diamondoids in petroleum condensates that were blocking pipelines for natural gas from Chevron's offshore platforms in the Gulf of Mexico. Again, the explanation for this phenomenon involves volatility, paradoxically associated with high melting point and low solubility. Dahl, Carlson and their associates succeeded in perfecting the technology for isolating and purifying diamondoids taking advantage of their higher thermal stability and resistance to oxidation in comparison with other petroleum hydrocarbons (Dahl et al. 2003). Reactions of diamondoids were studied by Schreiner and coworkers

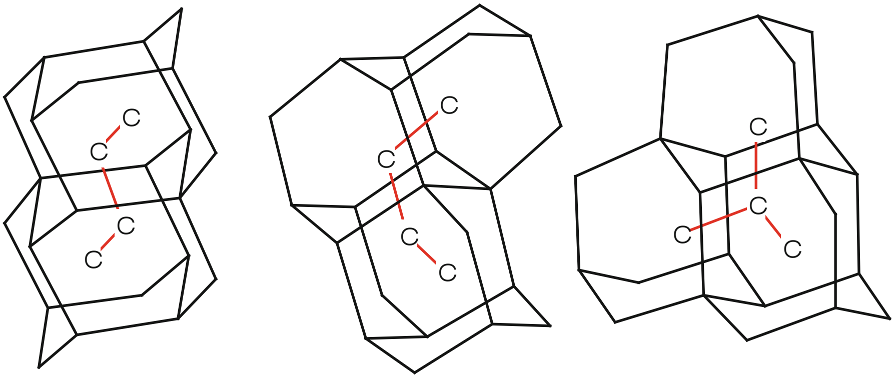


Fig. 1.5 Isomeric tetramantanes: [121]tetramantane, [123]tetramantane (one of the two enantiomers), and [1(2)1]tetramantane with branched dualist. Dualists are represented by *red* edges connectiung the centers of adamanane units indicated by letters C

Table 1.2 Regular catamantanes with $n = 4, 5, 6$, and 7 adamantane units. Upper row: *quaternary-tertiary-secondary* carbon atoms; lower row (red color): degrees of dualist (1, 2, 3, and 4)

n	C	Formula	Zero branches	One branch	Two	branches	Three branches
3	18	$C_{18}H_{24}$	1-10-7 **2**, 1, 0 0				
4	22	$C_{22}H_{28}$	2-12-8 **2**, 2, 0, 0	3-10-9 **3**, 0, **1**, 0			
5	26	$C_{26}H_{32}$	3-14-9 **2**, 3, 0, 0	4-12-10 **3**, 1, **1**, 0		6-8-12 4, 0, 0, **1**	
6	30	$C_{30}H_{36}$	4-16-10 **2**, 4, 0, 0	5-14-11 **3**, 2, **1**, 0	6-12-12 **4**, 0, **2**, 0	7-10-13 **4**, 1, 0, **1**	
7	34	$C_{34}H_{40}$	5-18-11 **2**, 5, 0, 0	6-16-12 **3**, 3, **1**, 0	7-14-13 **4**, 1, **2**, 0	8-12-14 **4**, 2, 0, **1**	9-10-15 **5**, 0, **1, 1**

in collaboration with Carlson, Dahl, and their coworkers from Chevron. They studied how to obtain regioselective functionalization by substituting hydrogens from tertiary or secondary positions (Schwertfeger et al. 2008).

A highly symmetric *formula periodic table* of regular catamantanes results (Table 1.2).when considering all isomers in terms of the number n of adamantane units and the number b of branches in the dualist (Balaban 2013b). Diamondoids have partitioned formulas $C_Q(CH)_T(CH_2)_S$. Regular catamantanes have the following partitioned formula: $C_{n+b-2}(CH)_{2n-2b+4}(CH_2)_{n+b+4}$.The numbers of quaternary and secondary carbon atoms increase according to the number n of units and number b of branches, whereas the number of tertiary CH groups increases twice as fast. The three components of the triplet Q-T-S indicating the numbers of C, CH, and CH_2 groups, respectively, are:

$$Q = n + b - 2 = S - 6 \tag{1.1}$$

$$T = 2(n - b + 2) \tag{1.2}$$

$$S = n + b + 4 \tag{1.3}$$

Till now all possible [n]diamondoids with $n < 8$ have been enumerated theoretically (Balaban and Schleyer 1978), and their partitions have been discussed (Balaban 2012, 2013b). Computer programs for enumerating higher polymantanes are urgently needed. The present author collaborated with Klein, Dahl and Carlson in finding molecular descriptors for QSPR correlations with diamondoid chromatographic data (Balaban et al. 2007).

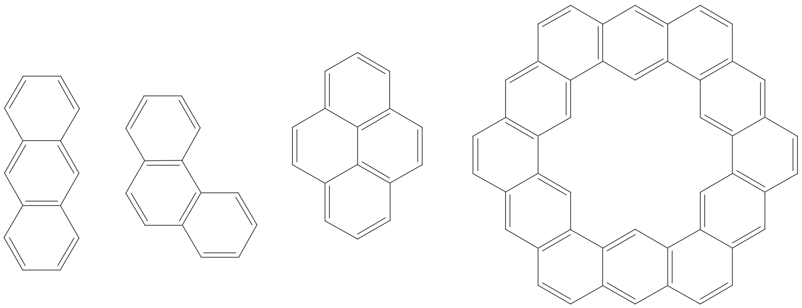


Fig. 1.6 Hydrogen-depleted structures of two catafusenes (isomeric anthracene and phenanthrene $C_{14}H_{10}$), one perifusene (pyrene, $C_{16}H_{10}$), and one coronafusene (kekulene, $C_{48}H_{24}$).

1.6 A Soft Carbon Allotrope, Graphite; Graphene; and Benzenoid Hydrocarbon Relatives

Naturally-occurring graphite is a soft, black carbon allotrope in which carbon atoms have sp^2 hybridization with interatomic distances of 1.41 Å, and form huge planar sheets stacked upon one another with inter-sheet distances of 3.35 Å, which are rigid in two directions but may glide in the third spatial direction, explaining thereby the low hardness (see Table 1.1). Geim's and Novoselov's discovery that one can isolate such one-atom thick sheets was honored with the 2010 Nobel Prize in Physics. Again, now for the different sp^2 hybridization, the graphene sheet is the perfect lattice, both as far as bond angles are concerned, and taking aromaticity into account. Graphene properties, especially the electrical conductivity, are astounding (Geim 2009).

Aromaticity started with August Kekulé, and was subsequently developed by well-known chemists, too many to mention (Balaban 1980; Randić 2003; Balaban et al. 2005). There are two ways of defining benzenoid hydrocarbons (or benzenoids, for short): (i) a restrictive definition, as planar fragments of the graphene lattice, and (ii) a more relaxed definition, which includes non-planar helicenes, and considers just the presence of benzenoid rings sharing CC bonds. The traditional classification into cata-condensed and peri-condensed benzenoids (or for short catafusenes and perifusenes, respectively) was based on the absence or presence of internal carbon atoms, respectively. A simpler and more comprehensive classification was advanced (Balaban and Harary 1968; Balaban 1969) on the basis of dualists (centers of hexagons, connected by an edge for adjacent hexagons sharing a CC bond): catafusenes, perifusenes, and coronafusenes have dualists that are acyclic, contain triangles, or larger rings that are not perimeters of triangle aggregates, respectively. The examples for all these types of benzenoids presented in Fig. 1.6 are all crystalline colorless compounds.

According to Erich Hückel, on the basis of quantum-chemical arguments, whenever the perimeter of a monocyclic or polycyclic benzenoid catafusene has an odd number of double bonds (i. e. $4n+2\pi$-electrons with $n=0$, 1, 2, etc.), enhanced

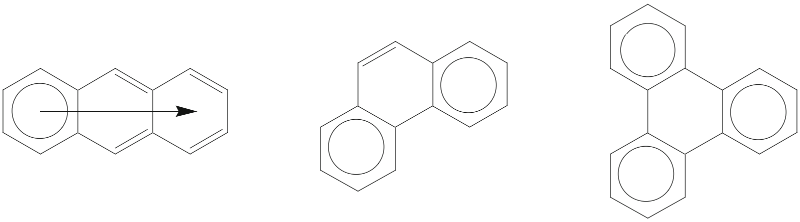


Fig. 1.7 Clar structures of anthracene, phenanthrene, and triphenylene

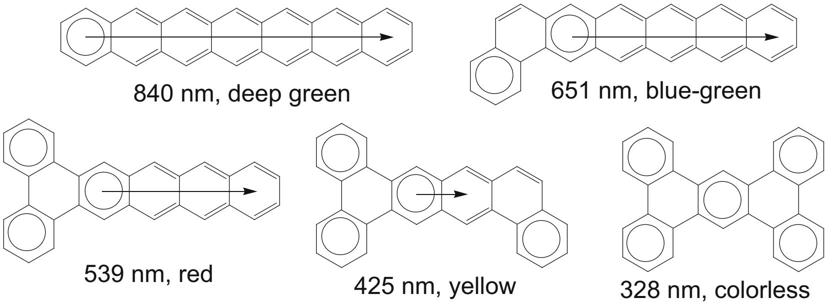


Fig. 1.8 Heptacatafusene isomers $C_{30}H_{18}$ with increasing numbers of Clar sextets from 1 to 5: longest absorption wavelength (in *nanometers*), and corresponding color

stability and many other characters associated with aromaticity are present. *Hückel's $4n + 2\pi$-electron rule* as a necessary and sufficient condition for planar aromatic systems applies also to ionic and to heterocyclic structures. For the simplest benzenoid, benzene, which has a π-electron sextet and is the prototype of perfect aromaticity, one can write two Kekulé valence structures. For [k]acenes with k linearly condensed benzenoid rings one can write $n + 1$ Kekulé structures, but for kinked benzenoids such as phenanthene or branched ones such as triphenylene, the number of Kekulé structures is higher.

Sir Robert Robinson invented formulas with a circle symbolizing a π-electron sextet. Eric Clar observed that electronic absorption spectra of benzenoids, which account for the colors of these hydrocarbons, are correlated with formulas (nowadays called Clar structures) using the sextet circle under the assumption that in polycyclic benzenoids there is a tug-of-war between rings trying to own π-electron sextets (Clar 1972). In acenes, the unique Clar sextet can move along and this is symbolized by arrows, as seen in Fig. 1.7. Clar formulas must have the maximum possible number of sextet rings; a ring can either have a sextet, or one or two double bonds; no sextets can be written in adjacent rings.

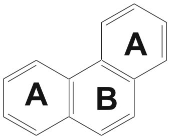
In Fig. 1.8 one can see Clar structures of five isomeric heptacatafusenes, starting with heptacene which absorbs red photons (and is therefore colored deep green, having $k = 7$ and 1 Clar sextet), and ending with tetrabenzanthracene which has 5 Clar sextets and absorbs only in the ultraviolet region and is therefore colorless.

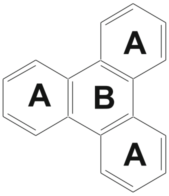
Table 1.3 Various kinds of partitions of π-electrons in two benzenoids

Hydrocarbon	Phenan threne		Triphe nylene	
Partition	A-ring	B-ring	A-ring	B-ring
Equipartition	5.00	4.00	5.00	3.00
π-Electron partition	5.20	3.60	5.33	2.00
Clar partition	6.00	2.00	6.00	0.00

Not only color, but also several other properties of polycyclic benzenoids can be correlated with two simple parameters: the number of benzenoid rings and the number of linearly-condensed rings: kinetics of cycloaddition with maleic anhydride (Balaban et al. 1985), redox potentials (Balaban et al. 2011; Singh et al. 2006), etc. (Balaban and Pompe 2007).

If one considers that each sp^2-hybridized carbon atom is associated with one π-electron, then equipartition would assign one π-electron to carbon atoms that are not shared to adjacent rings and 0.5 π-electrons when a carbon atom is shared with another ring. A more reasonable partition of π-electrons, reviewed in a book chapter (Balaban and Randić 2011), considers the average of all Kekulé valence structures weighted equally. Finally, Clar structures yield partitions according to the principle “winner takes all” (Balaban 2011). The 14 π-electrons of phenanthrene and the 18 π-electrons of triphenylene can be distributed according to the above types of partitions as shown in Table 1.3. By the same arguments, equipartition would assign two π-electrons to each carbon atoms in graphene because the sharing is between three rings.





1.7 The Newer Allotropes of Carbon: Fullerenes, Nanotubes, Nanocones, Nanotori

After the discovery of fullerenes by Smalley, Curl and Kroto (1996 Nobel Prize for Chemistry) by mass spectrometry (Kroto et al. 1985), it was possible to find experimental conditions for producing larger amounts of C_{60} and C_{70}, and for purifying them, arriving for the first time at *molecular carbon allotropes , i. e. at pure substances* containing exclusively carbon atoms (Krätschmer 1990). Buckminsterfullerene C_{60} is an assembly of carbon atoms arranged as a truncated icosahedron one,

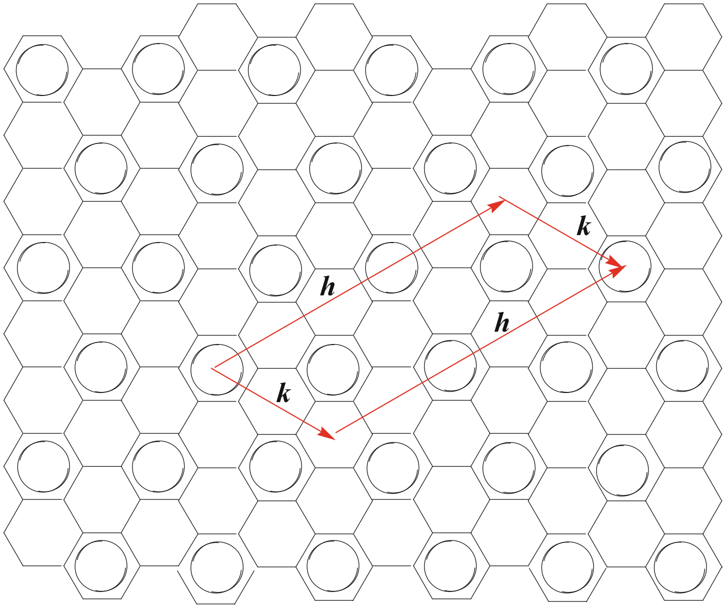


Fig. 1.9 Part of a graphene sheet with $h = 5$ and $k = 2$ vectors between two "sextet" hexagons

of the 13 Archimedean semiregular polyhedra. Higher fullerenes can be multiple-walled ("onion fullerenes"), or ellipsoidal double-capped nanotubes. Long nanotubes (Ijima 1991) have more complicated geometries (zigzag, armchair, chiral) and so far have been obtained only as mixtures. The same is true of nanocones (Balaban 2005; Klein and Balaban 2006) and nanotori (Klein and Balaban 2006). An interesting aspect of nanotubes is that their electrical conductance depends on the orientation of benzenoid rings with respect to the nanotube axis. It was shown that a simple rationalization of these experimental and theoretical data could be obtained by applying Clar's ideas to the folding of graphene sheets in forming single-wall nanotubes (SWNTs). Virtual Clar sextets in graphene must have conjugation along a poly-*para*-phenylenic direction, as seen in Fig. 1.9.

The folding obeys the vector rules (h, k) as indicated in Fig. 1.9 and Eq. (1.4). When $k = 0$, the folding occurs along an acenic portion leading to an achiral SWNT with a zigzag edge. In this case a congruent folding of Clar sextet rings occurs only if h is a multiple of 3. When $h = k$, the folding occurs along a poly-*para*-phenylenic direction affording also an achiral SWNT but now with an armchair edge. In this case a congruent folding occurs if $h - k$ is a multiple of 3. Otherwise (when $h \neq k \neq 0$) chiral SWNTs result, and congruent folding occurs only whenever Eq. 1.4 is fulfilled, which covers also the previous situations with achiral SWNTs.

$$h - k \equiv 0 \ (mod\ 3) \tag{1.4}$$

The resulting bandgap is zero (when curvature variations of the Hückel parameters are neglected) so that the nanotube will have a metallic conductivity, and otherwise it will behave as a semiconductor. As a result, all armchair SWNTs and one-third of zigzag and chiral SWNTs are metallic, whereas two-thirds are semiconducting (Klein and Balaban 2011).

1.8 Concluding Remarks

Having had for many years an interest in carbon nets, the present author witnessed many astonishing developments connected to the chemical element carbon. The aromaticity associated with sp^2-hybridized carbon atoms in certain cyclic structures is responsible for the amazing formation of fullerenes and nanotubes, as well as for the isolation of sturdy one-atom thick graphene sheets. The minimized electronic repulsion associated with staggered conformation of sp^3-hybridized C–C bonds is responsible for diamond being one of the hardest materials, for the presence of diamondoid hydrocarbons (diamondoids) in petroleum, and for the promising semiconductors obtained by epitaxial deposition yielding diamond-like films. The discovery of methods to isolate and purify naturally occurring diamondoids opened new perspectives for using such hydrocarbons in various applications after functionalization.

However, most praise should be addressed not to the element carbon, but to its compounds. Already from the infinity of chemical compounds, more than 7×10^7 organic substances have been characterized and registered, and they are by far more numerous than compounds of all other elements heavier than hydrogen. It is not due to chance that life is based on carbon compounds. What is amazing is that the element carbon with an abundance of only 0.08 % in the accessible earth's crust, oceans, and atmosphere (14th place among all elements) in its most oxidized form of carbon dioxide can be converted (at all latitudes on land or in oceans by bacteria, algae, and plants using water vapor and sun's energy) into carbohydrates and oxygen, thanks to the elaborate machinery of photo-assimilation. In the not too distant future, when mankind will have exhausted all fossil fuels (oil, coal, and natural gas) returning the element carbon to the climate-foe CO_2 due to greenhouse-effects, much more energy will be needed to make foods, plastics, and textiles by gaining access to carbon from calcium carbonate rocks. Will we be ready?

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