

Carbon allotropes: a suggested classification scheme based on valence orbital hybridization

R. B. HEIMANN^{a*}, S. E. EVSYUKOV^b and Y. KOGA^c

^aChair of Technical Mineralogy, Freiberg University of Mining and Technology,
D09596 Freiberg, Federal Republic of Germany

^bA.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
117813 Moscow, Russia

^cLaser-induced Reaction Laboratory, National Institute of Materials and Chemical Research,
Tsukuba, Ibaraki 305 Japan

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The importance of elemental carbon in modern science and technology is difficult to overestimate. A quarter century ago, Walker pointed out that the "progress in the development of new carbon materials will continue to be recorded - as a chapter in the over-all story of materials science" [1], and then continued to refer to carbon as an "old but new material". This expression did not lose its actuality but, on the contrary, is becoming even more topical today. Apart from the fact that life itself is based on the chemistry of carbon compounds, numerous technological applications of elemental carbon attest to its paramount importance to civilization. Further progress in the science of carbon promises to yield many unexpected and fascinating discoveries in the years to come.

Until the early sixties it has been generally held that the only carbon allotropes in existence were the naturally occurring three- and two-dimensional carbon polymers, i.e., diamond and graphite, respectively. Even "amorphous carbon", for a long time, was included among the simple forms. Currently, however, the structures of amorphous and quasi-amorphous carbons, carbon blacks, soot, cokes, glassy carbon, etc. are known to approach that of graphite to various degrees [2-5]. However, it was perceived rather illogical and puzzling by many researchers in the field that the element with the richest chemistry of all should be limited to just two allotropes. Apparently, the "missing link" in the story of carbon allotropy was a one-dimensional (chain-like) polymer, discovered by Russian scientists in 1960 and coined, rather unfortunately, "carbyne" [6]. (The term "carbyne" conflicts with the IUPAC term for an organic radical [7]). The increasing information gained on carbyne has been collected in several recent review papers [8-11]. In addition, from time to time publications appear proposing new crystalline forms or allotropic modifications of carbon [12-19]. Recently, the discovery [20] of a large family of spheroidal closed-cage carbon molecules termed fullerenes has added new excitement to carbon science [21-23]. Consequently, they were set apart as an independent (often called the "third" [24-26]) allotropic form of carbon.

In order to deal with the apparently inflationary number of proposed carbon allotropes, two questions now arise: (i) in how many independent forms can elemental carbon exist, and (ii) which are the criteria to distinguish these forms from the great multitude of other

carbon materials? *Allotropy* is the phenomenon of the existence of an element in a crystalline solid state in at least two distinct forms that differ from each other by the spatial arrangement of their atoms [27]. This definition, however, overlaps with notions of polymorphism and polytypism [28-29]. While the term "allotropy" refers to an alteration of the equation of state (EOS) of a substance and, therefore, should be used exclusively in a thermodynamic sense, the term "polymorphism" has, in addition, a crystallographic connotation, i.e. deals with structural and morphological changes. A particular case of one-dimensional polymorphism, characteristic of some closed packed and layered structures, is called *polytypism*. Polytypism is the ability of a substance to crystallize in several different modifications having two identical unit cell parameters whereas the third is variable, and most often an integer multiple of the distance between adjacent layers. Polytypism frequently occurs in structures equivalent to cubic and hexagonal closest packing of atoms. Since such structures have the same nearest neighbour atomic environment but differ in the character of the second (or even more remote) coordination sphere, they possess (almost) the same values of lattice energy and, consequently, very similar physical properties. Summing up, the definition of allotropy given above ought to be restricted, for carbon in particular, by adding the type of chemical bonds between the atoms as a distinguishing feature. Indeed, using Addison's definition [27] *sensu lato* would result in an enormous and ever increasing number of carbon allotropes.

To avoid this undesirable situation, a most convenient classification scheme for all carbon materials would be to distinguish them in accordance with the type of chemical bonds between carbon atoms, i.e., according to the type of hybridization of the valence orbitals [30]. Carbon atoms are known to exist in three states corresponding to sp^3 -, sp^2 -, and sp -hybridization of their valence orbitals. Each unique valence state belongs to a distinct archetypical, i.e., generic allotropic form that is characterized by its polymeric connectivity. Hence, the sp^3 -type of hybridization corresponds to a spatial (3D-) polymer of carbon, i.e., diamond. The sp^2 -type of hybridization corresponds to a planar (2D-) polymer, i.e., graphite. Finally, the sp -type of hybridization corresponds to a linear (1D-) chain-like polymer of carbon, i.e., carbyne. According to this classification, fullerenes and their derivatives have to be

considered zero-dimensional since their closed-cage molecules do not lend themselves to polymeric structures connected by directional bonds but only to van der Waals-type interactions. In addition, each of these three polymeric carbon allotropes reveals polymorphic as well as polytypic structures [31]. Diamond exists as a cubic polymorph (CIII), hexagonal polymorph (CIV, lonsdaleite, δ -phase, diamond polytype $2H$), as well as the hexagonal diamond polytypes $8H$, $12H$, $16H$, and $20H$. Graphite exists as a hexagonal polymorph with ABAB-stacking (also called CI, α -graphite, $2H$ -graphite), a rhombohedral polymorph with ABCA-stacking (also called CII, β -graphite, $3R$ -graphite), and the polytypes $6R$, $10H$, and $12H$. There also seems to exist a second hexagonal graphite form (CVII) with A-over-A stacking corresponding to a $1H$ -polytype [32]. Finally, hexagonal carbyne so far exists only in polytypic forms, i.e., as α -carbyne, β -carbyne, chaoite (CV), CVI, CVIII-CXIII [33-35]. The Roman numbering scheme of carbon forms used above has been introduced by Whittaker [36] but is not without its ambiguities. The polytypic carbyne forms are distinguished by their different chain lengths some of which are presumably related to their formation temperature [33-35, 37].

Whereas diamond and graphite have been the subject of comprehensive studies and reviews [38-39], no rigorous and structurally unambiguous evidence of the existence of carbyne is available yet. Notwithstanding the large number of studies published [8-11], carbyne was not included in a list of terms recently recommended by IUPAC for the description of carbon as a solid [40]. However, based on a critical review of the whole body of experimental data accumulated to date [41], new analytical techniques and modeling approaches being currently available [42-44], and the increasing interest among scientists in these fascinating structures as evidenced by a proliferation of experimental and theoretical papers, the existence of carbyne should be irrefutably established in due course.

All other forms of elemental carbon apart from those mentioned above constitute the vast body of so-called transitional forms [5] that, in turn, can be divided into two groups. The first group comprises mixed short range-order (SRO) carbon forms of more or less randomly arranged carbon atoms of different hybridization states, including various ill-defined carbon materials such as "amorphous" carbon, diamond-like carbon (DLC) and vitreous carbon, as well as various carbon blacks, soot, cokes, etc. Numerous hypothetical structures such as graphynes [45], some polycyclic 3D-carbon networks [46-52] including "metallic carbon" [47] and related structures incorporating allenic [48] or diacetylenic [53-54] links between orthogonal sp^2 -chains, hinged polydiacetylene carbon phases [49] referred to as twisted-chain auxetics owing to their predicted negative Poisson's ratio, "superdiamond" [53-54], and layer-chain carbons [55-57] (i.e., carbyne-diamond hybrid structures being in effect the particular case of 1D-"superdiamond") can also be assigned to the mixed forms of carbon. Synthetic strategies towards such mixed forms have been rather exhaustively reviewed by Diederich and Rubin [53-54].

The second group includes intermediate carbon forms. The degree of hybridization of carbon atoms in these forms can be expressed as sp^n , where "n" is non-integral but a fractional number ($1 < n < 3$, $n \neq 2$). This group, in turn, can be divided into two subgroups. The

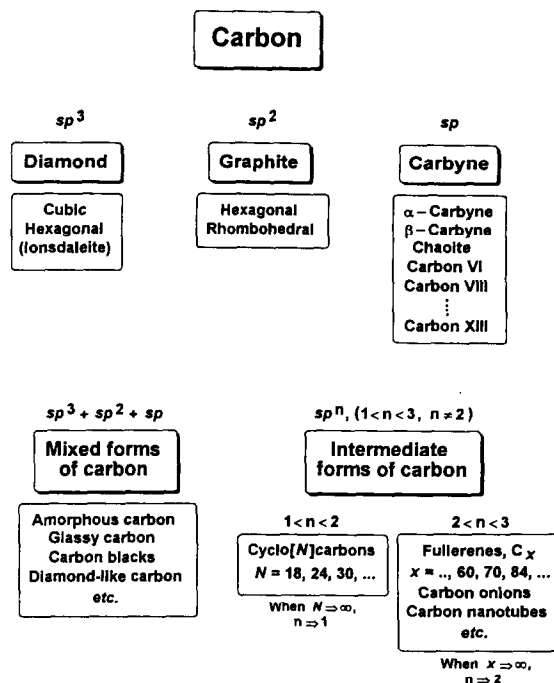


Fig. 1 Classification scheme for carbon allotropes.

first one ($1 < n < 2$) includes various monocyclic carbon structures like cyclo[N]carbons reported by Diederich et al. [58-59]. For $2 < n < 3$, the intermediate carbon forms comprise various framework (or closed-shell) carbon structures such as fullerenes [8], carbon onions [60-62] and nanotubes (giant "linear fullerenes") [63-65], hypothetical C_{120} torus [66] and fullereneynes [67-68], as well as related diamond-graphite hybrid structures [69-70]. The fractional degree of hybridization found in intermediate carbon forms is due to the curvature of their frameworks causing the carbon skeleton to be strained [71-72]. Therefore, for instance, the degree of hybridization of carbon atoms in C_{60} , the most in-depth studied member of the fullerene family, was reported to be 2.28 [71]. Some polycyclic carbon networks can also be assigned to the intermediate forms provided they contain strained cycles in their structure [73-76]. In some particular cases, however, one should take into account electronic interactions in the system along with geometric parameters. For example, the network of "metallic carbon" consisting of regularly cross-linked puckered layers of orthogonal polyene chains is free from angle strain [47], whereas it is not free from " π -strain". The π -clouds of neighbouring polyenes are forced by the cross-links to be much too close to each other, thereby making the entire structure metallic.

The general classification scheme for carbon allotropes is given in Fig. 1, and a related tentative ternary carbon allotropy diagram[‡] based on carbon valence bond hybridization is shown in Fig. 2. This figure includes confirmed, hypothetical, and speculative allotropes (corners of triangle) and transitional forms of carbon (both mixed and intermediate) located at the edges and inside of the triangle. Carbon forms with sp^n

[‡] This idea has been first publicly suggested at a seminar given by RBH at the National Chemical Laboratory for Industry (NCLI), Tsukuba, Japan on May 28, 1992.

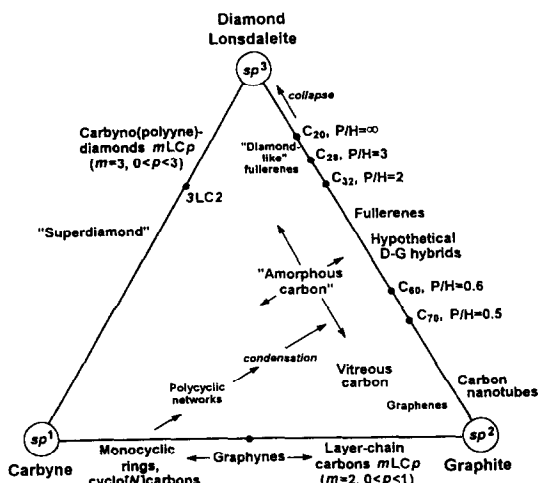


Fig. 2 Ternary "phase" diagram of carbon allotropes.

hybridization ($2 < n < 3$) are located along the sp^2 – sp^3 edge of the triangle, showing for C_x fullerenes the ratio of pentagonal to hexagonal rings (P/H), with $P/H = 0$ corresponding to pure graphite and $P/H = \infty$ corresponding to an all-pentagonal ring cluster C_{20} of a "diamond-like" fullerene that has been shown, by the expanded Hückel method, to have an electron shell that is not closed [77–78]. Because of a violation of the isolated pentagon rule (IPR), it is unstable and thus ought to collapse into the diamond structure. Indeed, the deposition of carbon clusters with selected size distribution around C_{20} produced using a laser vaporization source was reported to afford diamond-like carbon with nearly pure sp^3 -hybridization [79]. This conjectured collapse of low-mass fullerenes $<C_{32}$ could explain the conspicuous absence of TOF-MS peaks below $x=32$ in sooting oxygen/acetylene flames [80–81], and may be the driving force for diamond formation by the Hirose process [82–83]. Carbon forms with a degree of hybridization conforming to $1 < n < 2$ include mono-cyclic cyclo[N]carbons with $N = 18, 24, 30, \dots$ [58–59, 84]. The reactions of such cyclocarbons have been proposed to play a key role in the formation of fullerenes. The coalescence of planar carbon rings [85–86] produces new polycyclic species that can either grow further or anneal to give fullerenes or larger monocyclic rings [87–88]. The latter, in turn, can participate in subsequent condensation reactions or act as nuclei in the formation of carbon nanotubes [89]. Polyene chains spiraling around fused aromatic fragments can "zip up" to form fullerenes [87–88]. Similarly, long polyene chains terminated by delocalized electrons may roll up in a spiral fashion to generate fullerenes via a series of zipper-like reactions [43].

Highly strained polycyclic networks with a high degree of condensation will give rise to graphynes [45], planar sheets in which one-third of the carbon bonds in graphite 6-rings are replaced by sp -hybridized $-C\equiv C-$ linkages. While the stacked carbon layers in graphyne are held together by interlayer van der Waals interactions as in graphite, hypothetical carbyne-graphite hybrid forms that are attributable to so-called layer-chain carbons, $mLCp$ ($m = 2, 0 < p < 1$), are thought to consist of highly strained graphite layers partially connected by short chains extending along the crystallographic c -axis [57].

The third (sp^3 – sp) side of the triangle in Fig. 2 is currently much less defined. Besides the archetypical sp^3 allotropes, viz., diamond and lonsdaleite, there is a suggestion of an all- sp^3 -carbon atom allotrope with a density exceeding that of diamond, called supercubane or C_8 [12]. The originally anticipated carbon bond lengths of 0.142 nm (intracube) and 0.123 nm (intercube) were considered too short for sp^3 -hybridization so that an alternative BC-8 (analogous to high pressure γ -Si) structure has been proposed with an intracube bond length of 0.154 nm and a twisted boat-conformation of the carbon 6-rings to account for denser packing compared to diamond [75]. Furthermore, carbyno(polyyn)-diamond corresponding to the above-mentioned 1D-"superdiamond" (layer-chain carbon, $mLCp$ with $m = 3$ and $p = 2$), was proposed to consist of puckered diamond-like layers in which fused carbon rings with chair-type conformation (*trans*-decalin) are regularly linked to each other by short sp -type carbon chains perpendicular to the layers [55–57]. Such hypothetical structures were suggested to be transient phases during the transformation of graphite to diamond mediated by a passing shock wave [90] in analogy to the collapse pattern invoked by Hoffmann et al. [91] of strain-free carbenoid biradicals, i.e., sp^3 -cyclohexane rings connected by triangular nets of linear sp -diradicals (carbenes). Finally, a 3D-"superdiamond" lattice may exist [53–54] in which all single carbon bonds in the chair-type rings are connected by butadiene segments.

Carbon forms located inside the triangle (Fig. 2) are those having bond contributions of all three types of hybridization in various combinations. They belong mostly to mixed carbon forms specified above, in particular amorphous and vitreous carbon (glassy carbon with sp^2 dominance) [3, 92–95]. One can expect, however, that really existing complex carbon materials (diamond-like, glassy and amorphous carbon, soot, carbon blacks, cokes, etc.) may incorporate structural elements with randomly distributed intermediate hybridization states.

The structure and amount of these elements should depend on the method and conditions of synthesis. Other conceivable forms of carbon include even more complicated materials consisting of structural elements of both mixed and intermediate forms. Such materials can be produced, for example, by polymerization (cross-linking) of fullerene molecules [96–98] as well as during shock-induced transformations of fullerenes into diamond [99–103], graphite [104], or carbyne (chaoite) [105].

In conclusion, in this letter an attempt has been made to group the inflationary number of members of the carbon allotrope "zoo" reported hitherto into:

- (i) "archetypical" allotropes with an integer degree of carbon bond hybridization, i.e., diamond, graphite, and carbyne; and
- (ii) transitional carbon forms that include:
 - (a) mixed SRO carbon forms with randomly arranged carbon atoms of different hybridization states, e.g., amorphous carbon, diamond-like carbon, vitreous carbon, soot, carbon blacks, etc., as well as numerous hypothetical structures like some polycyclic carbon networks, graphynes, layer-chain carbons, "superdiamond"; and
 - (b) intermediate forms with a non-integer degree of carbon bond hybridization, sp^n , e.g.,

cyclo[*N*]carbons, fullerenes, carbon anions, nanotubes, and related structures.

From this classification scheme it also follows that carbyne instead of fullerene should be considered the third allotrope of carbon [10]. To represent graphically both the unity and the variety of the carbon forms within this framework, a ternary "phase" diagram of carbon bond hybridization is proposed.

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A phase transition between carbon allotropes synthesized by a combustion-flame method

J.F. DESPRES, H. OKUNO, H. TAKAHASHI and O. ODAWARA.
Department of Materials Science and Engineering, Tokyo Institute of Technology,
4259 Nagatsuta, Midori-ku, Yokohama 226, JAPAN

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In the previous paper [1], peculiar carbon textures have been obtained by an oxy-acetylenic combustion flame method. These species were called "gypsum flower"-like carbons (GF) because of the resemblance to gypsum crystallization in the Sahara. One variety of these peculiar textures has been already found by others scientists using different techniques such as arc discharge [2]. Therefore, the GF texture should be a full member of any carbon microstructure diagram, established with such non-equilibrium reaction products, as well as diamond. Nevertheless, no phase characteristic in the carbon phase diagram related to the flame method has been accurately defined. Mixing phases of diamond-like and diamond or GF species has been easily performed.

In the recent literature, many authors have shown that the formation of diamond can occur not only by shock compression [3], but also by various techniques

directly from various carbon species [4-8]. Others have produced computer calculations of the plausible transition between graphite and diamond [9,11]. Nevertheless no results exhibit the possible mechanism of the transition. Consequently, because of the blurred dividing lines in the flame synthesis carbon phase diagram, we have sought a route to get directly to diamond from GF. In this way, we used GF-like carbon to check the possibility of getting sp^3 carbon directly from the sp^2 phase. We report here some of our which show the possibility of producing diamond from GF.

The present experiments have been carried out with the same equipment described in the previous work [1] under atmospheric pressure in air. The O_2/C_2H_2 ratio of the flame was around 0.9 with O_2 and H_2 gas flows of 1.6 l/min. and 1.5 l/min. respectively. Silicon and molybdenum were used as the substrates, while