



**HAL**  
open science

## Elemental carbon in the $sp^1$ hybridization

Florian Banhart

► **To cite this version:**

Florian Banhart. Elemental carbon in the  $sp^1$  hybridization. ChemTexts, 2020, 6 (1), pp.3.  
10.1007/s40828-019-0098-z . hal-03603814

**HAL Id: hal-03603814**

**<https://hal.science/hal-03603814>**

Submitted on 10 Mar 2022

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Chem. Texts (2020) 6:3

<https://doi.org/10.1007/s40828-019-0098-z>

## Elemental carbon in the $sp^1$ -hybridization

Florian Banhart<sup>1</sup>

<sup>1</sup> Université de Strasbourg, CNRS, Institut de Physique et Chimie des Matériaux, UMR 7504, 67034 Strasbourg, France

[florian.banhart@ipcms.unistra.fr](mailto:florian.banhart@ipcms.unistra.fr)

### Abstract

The hybridizations of the carbon atom are textbook examples for different types of chemical bonds. Likewise, the elemental phases of carbon, graphite and diamond, are well known as materials in the pure  $sp^2$  or  $sp^3$  hybridization. However, what is much less known is the elemental carbon phase in the  $sp^1$  (or  $sp$ ) hybridization. The phase is called carbyne and still somewhat elusive, although many reports about successful syntheses have been given. Carbyne is assumed to consist of densely packed linear chains of carbon atoms and appears to be a rather unstable material. Individual chains of carbon atoms are perfectly one-dimensional structures and show many highly interesting physical properties of classical 1D materials. This article first gives an overview over the relation between the differently hybridized elemental phases of carbon and then focuses on the structure and the properties of individual  $sp^1$  chains of carbon atoms. A brief survey of the synthesis of individual carbon chains as well as bulk carbyne is given at the end of the article.

### Keywords:

Carbon allotropes, carbyne, carbon chains,  $sp$ -hybridization, one-dimensional materials

## Introduction: The phases of elemental carbon

Carbon is an element that occurs in modifications with completely different forms of appearance. Everyone knows graphite and diamond as the prime examples for the diversity of the phases of one and the same element. While graphite is a black, soft and electrically conductive solid, diamond comes in the shape of transparent, hard and insulating crystals. This diversity is not just due to the different crystal structures of graphite and diamond but to the different electronic states of the carbon atom, allowing it to form three or four covalent bonds to its neighbours.

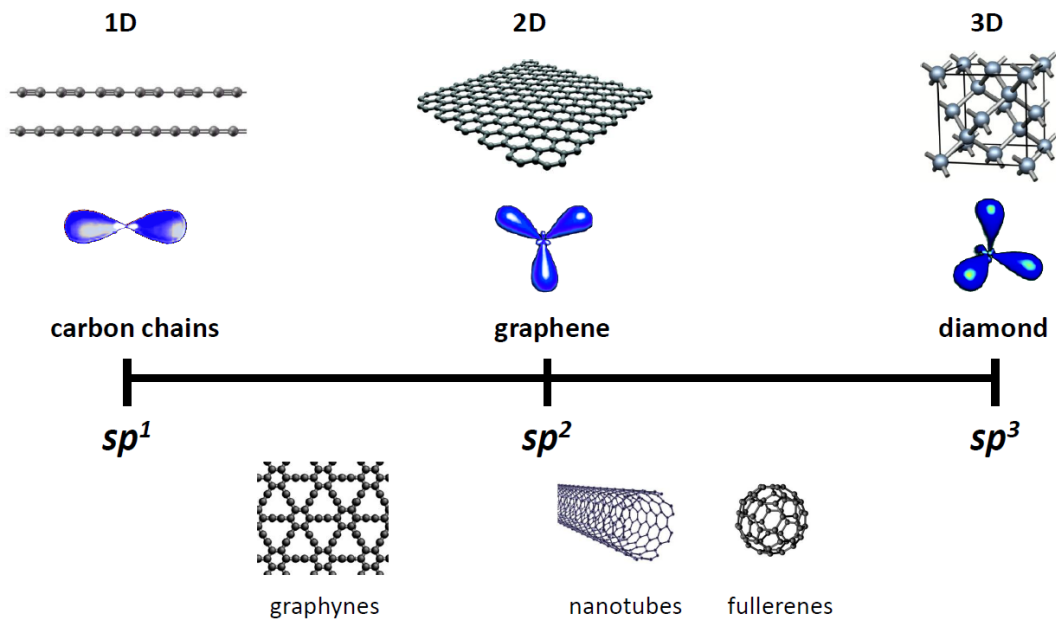
The formation of an elemental structure larger than a dimer needs at least two bonds per atom. Indeed, there exists such a carbon modification where every atom is linked to only two neighbouring atoms. However, this phase is much less known than graphite or diamond. This exotic form of carbon is called *carbyne* or *linear acetylenic carbon* and known since many decades [1, 2]. To date, only minor quantities of **bulk** carbyne have been synthesized since it turned out to be rather reactive and unstable against relaxation into graphite. Traces of carbyne have been found in shock-compressed graphite and in meteorites and it is even suspected to be present interstellar dust. Despite its elusive appearance, carbyne is a highly interesting model system to study perfectly one-dimensional materials.

The key for understanding the different carbon modifications, not only in elemental carbon but also in many carbon compounds, is the principle of hybridization. In the electronic ground state of the carbon atom, the 2s-orbital is filled with two electrons of antiparallel spin while the 2p-orbital has two electrons with parallel spins, one in the 2p<sub>x</sub>- and one in the 2p<sub>y</sub>-orbital. This is due to Hund's rule, saying that the repulsion of electrons on orbitals of the same energy (here p-orbitals) is less if the spins are parallel. However, the electron wavefunctions  $\Psi_{2s}$  and  $\Psi_{2p}$  can be combined so that a hybrid wavefunction  $\Psi_{\text{hyb}} = C_1 \Psi_{2s} + C_2 \Psi_{2p}$  is obtained ( $C_1$  and  $C_2$  are constants). The degeneracy of the four hybrid orbitals is broken once chemical bonds with neighbouring atoms form. The hybridization of the orbitals needs energy which is retrieved or overcompensated by the formation of chemical bonds with other atoms.

The new hybrid orbitals allow up to four equivalent bonds per carbon atom. In the  $sp^3$ -hybridization, all four hybrid orbitals are able to form covalent bonds and the repulsion between the orbitals leads to a tetrahedral alignment of the bonds (Fig. 1). Covalent bonding with neighbour atoms leads to a periodic arrangement of atoms which is (in the most stable modification) a crystal known as cubic diamond. In the  $sp^2$ -hybridization, only three hybrid orbitals exist and form covalent  $sp$ -bonds with neighbours and one p-electron is left over and forms a p-orbital. This leads to a bonding geometry where all three covalent  $sp$ -bonds are aligned in a plane with an angle of 120° between them and gives the well-known hexagonal lattice of graphene, which is a perfectly two-dimensional structure. However, stacking of the graphenic planes with their two-dimensional  $\pi$ -electron system on both sides leads to weak inter-planar bonding of van der Waals type and to graphite as the bulk phase of  $sp^2$ -carbon. Finally, the  $sp^1$ -hybridization only allows two hybrid orbitals that form

covalent bonds in opposite directions and results in a linear chain of carbon atoms. (This hybridization is often denoted just as  $sp$  but we will use the term  $sp^1$  to avoid confusion with  $sp$ -hybrid orbitals.) The two remaining p-orbitals per atom form a  $\pi$ -electron system along the chain. Stacking of the chains in two dimensions leads to bulk carbyne.

The relation between the different hybridizations of carbon and the corresponding modifications is shown schematically in Figure 1. The three modifications of carbon, each defined by its type of hybridization, are model systems for low-dimensional materials. Diamond is a three-dimensional crystal due to the tetrahedral distribution of the four hybrid orbitals in 3D space and the formation of four strong covalent bonds. Graphene, on the other hand, is a perfectly two-dimensional structure (ideally an infinitely extended plane) since strong covalent bonds only exist in the plane. Graphene is the first 2D material with a thickness of one atom. Finally, carbon chains as the constituents of carbyne can be considered as one-dimensional structures of atomic thickness.



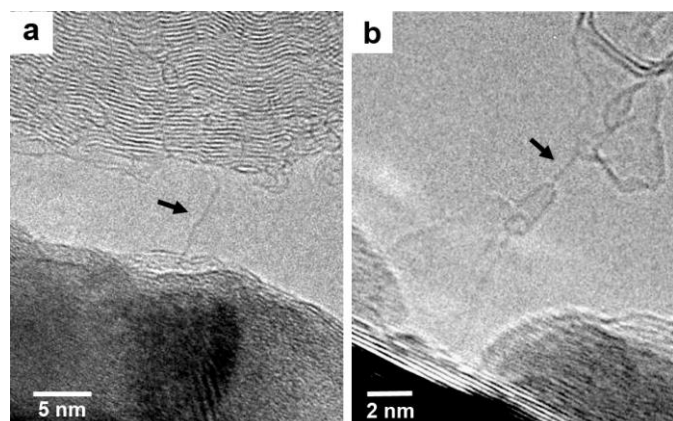
**Fig. 1** The hybridizations of carbon and the corresponding modifications. Pure hybridizations are shown above the line (chains, graphene, diamond). The  $sp$  hybrid orbitals forming covalent carbon-carbon bonds are drawn in blue. Some intermediate structures are shown below the line (graphynes, nanotubes, fullerenes).

It has to be pointed out that the hybridization of carbon atoms doesn't have to be strictly of one of the three types  $sp^1$ ,  $sp^2$  or  $sp^3$ . All intermediary mixed states are allowed as well (Fig. 1). Examples are graphenic structures where the planes are curved which is the case in fullerenes [3] whose hybridizations are between  $sp^2$  and  $sp^3$ . The  $sp^3$ -character increases with increasing curvature of the planes; e.g., carbon atoms in the  $C_{60}$  molecule have approximately 10%  $sp^3$ -character. More complex

structures with the appearance of different hybridizations of carbon do also occur such as in graphynes.

The covalent  $sp$ -bond in all carbon phases is very strong and has a length of 0.154 nm in diamond resp. 0.142 nm in graphite. The localization of electrons in the  $sp$ -hybrid orbitals of the covalent bonds does not allow charge transport. This is the reason why diamond, that consists of  $sp$ -bonds only, has a large bandgap (5.47 eV) and is therefore a perfect electrical insulator and optically transparent. Furthermore, diamond with its densely packed lattice is hard under mechanical load in all possible directions. Graphene (or graphite), on the other hand, has the overlapping  $p$ -orbitals forming the  $\pi$ -electron system which allows charge transport along the plane. Therefore, graphite is an electrical conductor and optically opaque. Strictly speaking, graphene as a monolayer of graphite is a zero-bandgap semiconductor and has low light absorption. Graphene is extremely tearproof in the plane but the weak van der Waals bonding between the planes of graphite through the  $\pi$ -electron system allows easy shear of the planes against each other (this happens in writing with a pencil). Similarly, chains of carbon atoms in the  $sp^1$ -hybridization are assumed to be extremely strong against rupture but can be slid easily against each other in two dimensions. The presence of delocalized  $\pi$ -electrons lets us expect that carbyne is an electrical conductor.

While the properties of diamond and graphite are known since centuries, most characteristics of  $sp^1$ -bonded carbyne are still hypothetical and based on calculations. It was just in the past years that new experiments shed more light onto individual carbon chains as the constituents of carbyne [4, 5]. In modern electron microscopes with high image resolution, such atomic wires are getting immediately visible. Figure 2 shows examples of electron microscopy images of carbon chains. In the following, we will discuss the structure and properties of  $sp^1$  carbon and give a brief overview of possible routes towards its synthesis.

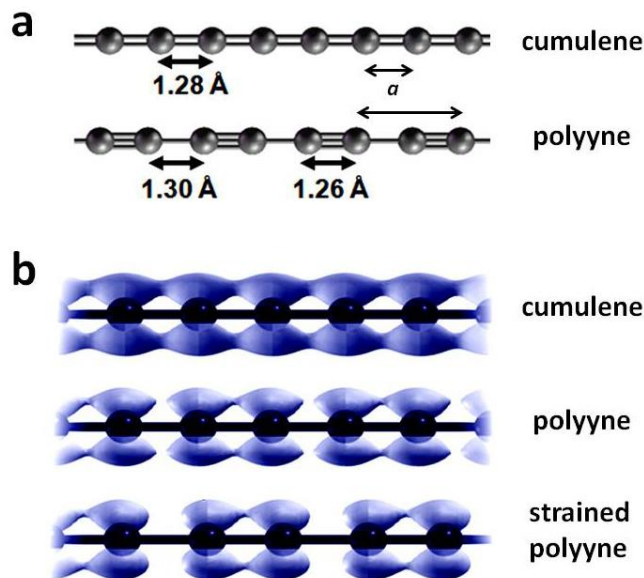


**Fig. 2** Transmission electron microscopy images of atomic carbon chains (arrowed) spanning between different contact points. The chain in **a** bridges the gap between a graphitic layer on a metal substrate (bottom) and a larger graphitic aggregate (top). The chain in **b** is attached to the end cap of a small carbon nanotube (bottom) and to a graphenic sheet (top).

## The model of linear carbon chains

If  $sp^1$ -bonded carbon atoms are arranged in a linear chain, the question of multiple carbon-carbon bonds arises. Taking  $sp^2$ -hybridized carbon as an example (like in graphene or benzene), it is common to denote the common contribution of a covalent  $sp$ -bond and a less localized  $p$ -orbital as a double bond. However, it has to be kept in mind that the concept of single, double and triple bonds is an elastic term and just an illustration of the number of electrons (more generally the electron density) contributing to the bond. It does not take into account delocalization effects, i.e., whether electrons are localized within a bond or delocalized over a larger distance. As we know from Kekulé's model, it is not possible to assign double bonds in benzene (and likewise in graphene) to certain atoms; instead, the  $\pi$ -electron system is uniformly distributed in a ring over the hexagon.

In a chain of  $sp^1$ -bonded carbon atoms, one covalent  $sp$ -bond and two  $p$ -orbitals contribute to bonding. It would therefore be obvious to draw a triple bond between two atoms. To ensure four bonds per atom throughout the chain and taking delocalization into account, either alternating single and triple bonds or double bonds over the whole chain are possible as shown in Figure 3. The first configuration  $-C\equiv C-C\equiv C-$  is called *polyynes* while the second  $=C=C=C=C=$  is known as *cumulene*. While the  $p$ -electrons in polyynes are localized on the triple bonds, their delocalization over the chain in cumulene leads to a metallic behaviour.



**Fig. 3** **a** Bond lengths and lattice parameters  $a$  in cumulene and polyynes. **b** Overlap of the  $p$ -orbitals in cumulene, polyynes and strained polyynes (courtesy of J.-C. Charlier).

To decide which of the two electronic configurations prevails under given conditions, electronic and elastic effects have to be considered. When a carbon chain transforms from cumulene to polyynes, the symmetry around each atom is broken and

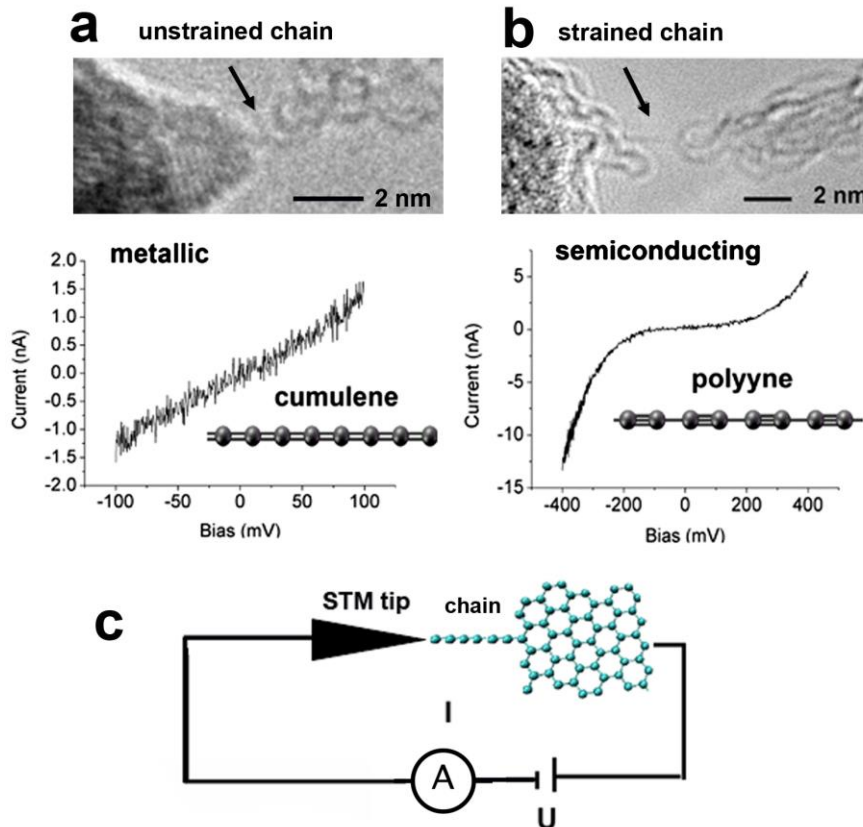
dimerization occurs. The one-dimensional lattice parameter  $a$  changes from the simple to twice the interatomic distance (Fig. 3a). The dimerization is reflected by the (calculated) bond lengths which are 0.1301 nm for the single bond in polyynes, 0.1282 nm for the double bond in cumulene and 0.1265 nm for the triple bond in polyynes [6]. A higher electron density between two atoms leads to a shorter bond. It has to be noted that the bond lengths in carbon chains are not exactly the same as in organic compounds with multiple carbon bonds. The single bond in polyynes is slightly shorter than the carbon-carbon bond in ethane while the triple bond in polyynes is longer than in acetylene.

Two contributions to the energy of the chain are of importance, namely the electronic energy which is given by the band structure and the strain energy which is determined by changes in bond length. Cumulene with its delocalized p-electrons can be considered as a perfect one-dimensional metal. According to a theorem of Peierls [7], linear metals are unstable against a distortion of the lattice periodicity which leads to dimerization. Since the electrons are localized over every second bond (the triple bond) and the neighbouring single bonds are depleted, charge transfer along the chain is impeded and can only occur when thermal energy allows hopping of charge over the single bonds. This behavior is described by the opening of a bandgap between the valence and the conduction band. The bandgap leads to a lowering of the electronic energy of the system and so to the stabilization of polyynes. However, it has recently been noted that a reverse contribution comes from zero point atomic vibrations that counteract Peierls distortion and stabilize cumulene [8].

The dimerization in polyynes [9] costs strain energy due to the formation of longer and shorter bonds. Externally applied mechanical strain leads to a preferential lengthening of the weaker single bonds which again favours dimerization and opens the bandgap even more [8, 10, 11]. It is therefore the balance between the contributions of electronic energy, zero point vibrations and strain that determines whether we find carbon chains in the cumulene or in the polyynes configuration. Another contribution to the bonding character may come from end groups attached to the chains. An end group imposes a single or a double bond that acts like a boundary condition and influences the other bonds in the chain.

To decide experimentally if a chain is cumulene or polyynes, the interatomic distances or the electrical conductivity can be measured. The interatomic distances have already been measured in an electron microscopy study, showing an unexpectedly strong dimerization where the difference in bond lengths (single vs. triple) is much higher than predicted [9]. In electrical characterization experiments, it has been found that unstrained chains are metallic conductors, as it is expected for cumulene, whereas strained chains show semiconducting behaviour which is typical for polyynes [11]. The two types of band structure can be easily distinguished just by measuring current-voltage curves in the chains. As shown in Fig. 4, metallic conductivity results in a linear I-V curve (ohmic behaviour) whereas semiconducting chains show a sigmoidal I-V curve. Further studies are necessary to refine the picture.





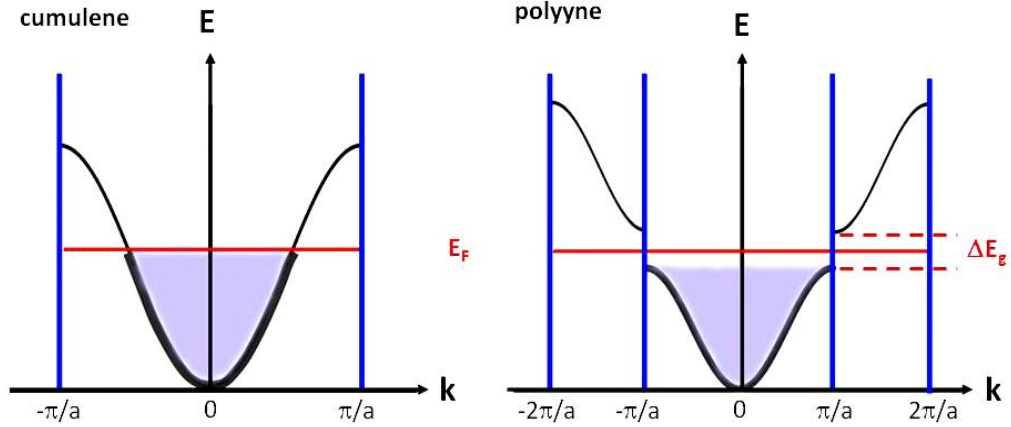
**Fig. 4** Current-voltage measurements in carbon chains. The warped chain in **a** shows a linear I-V curve which is typical for metallic (ohmic) resistivity and therefore attributed to cumulene. The chain in **b** is strained and shows the sigmoidal I-V curve of semiconducting polyyne. The arrangement for measuring the curves is drawn schematically in **c**.

### The physical properties of $sp^1$ -carbon chains

In the following, we will discuss the electrical, mechanical and thermal properties of individual carbon chains (an outlook on carbyne, consisting of an arrangement of chains, will be given in the next chapter). It has to be pointed out that only few properties have already been measured experimentally and the majority of information that we have today is still based on theoretical work.

The electronic band structure of the two modifications, cumulene and polyyne, is shown in Figure 5. Cumulene is metallic and the band structure has a simple parabolic shape. This is the textbook example of a one-dimensional metal. Since the lattice parameter  $a$  corresponds to the simple interatomic distance (see Fig. 3), the edge of the first Brillouin zone is at  $k = \pi/a$ . The conduction band, given by the overlapping p-orbitals, is half filled (shaded in blue) up to the Fermi energy  $E_F$ . In polyyne, the lattice parameter is twice the atom distance. The valence band in polyyne is completely filled and separated by a bandgap  $\Delta E_g$  from the empty conduction band. It has been shown that the width of the bandgap depends on the strain state of the chain [10].





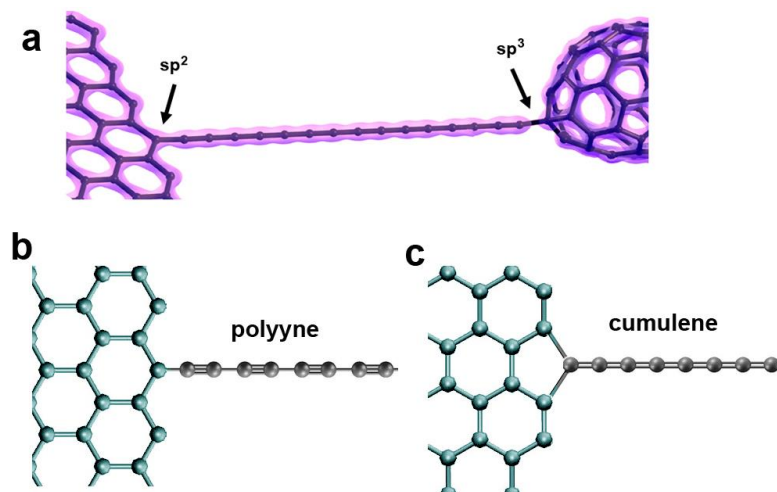
**Fig. 5** Band structures of cumulene and polyynes (electron energy  $E$  over the wave vector  $k$  in an extended zone scheme). The edges of the Brillouin zones are marked with blue vertical lines at multiples of  $\pi/a$ . The Fermi energy  $E_F$  is marked by red lines.

An important characteristic of carbon chains in view of possible applications as electrical wires is their electrical conductivity. Due to the atomic size of the chains, the principles of quantum conductivity have to be applied and electrical transport is calculated on the basis of the Landauer-Büttiker theory. An elementary conduction channel (the smallest and most elementary conductor) has a conductivity  $G_0 = 1/R_0 = 2e^2/h$  which is the reciprocal resistivity  $R_0$  and given by the elementary charge  $e$  and Planck's constant  $h$ . The factor 2 is due to two possible spin states. Accordingly, we find  $G_0 = 7.8 \times 10^{-5}$  S (corresponding to the inverse of the quantum resistance  $1/12.9$  k $\Omega$ ). However, we have the presence of two conduction channels in carbon chains due to conductivity over  $p_x$  and  $p_y$  orbitals (the chain is aligned along the  $z$ -direction) so that we have to multiply by another factor of 2 and obtain for the total conductivity of a chain  $G_{chain} = 2G_0 = 4e^2/h$ . As in graphene or carbon nanotubes, charge transport is expected to be ballistic. This consideration is valid for an idealized infinite chain. Unlike in a classical conductor, the conductivity doesn't depend on the length of the chain. For a finite chain spanning between two contacts, the formula has to be extended by a transmission factor  $T$  and a reflection factor  $R$  so that the conductivity is  $G_{chain} = 4e^2 T/hR$ . Here, the conductivity is limited by reflections of electron waves at the contacts and by stationary states given by the boundary conditions at the contacts.

The potential application of carbon chains as wires for interconnecting nanodevices also depends on the maximum current they can carry before failure. A current of approximately 6  $\mu$ A has been measured experimentally in a monoatomic chains at an applied voltage of 1.8 V which is an enormous current, given the atomic nature of the chain [12]. However, taking the above formula for an ideal infinite chain, a current of up to 300  $\mu$ A should be reached at 1.8 V. The limiting factors in a real experiment are the transmission and reflection factors that don't allow to reach the quantum limit  $2G_0$ .

Another interesting aspect of the influence of bonding on the electrical transport is the local hybridization at the end atoms. As shown in Fig. 6a, the end bonds in carbon contacts can be of  $sp^2$  or  $sp^3$  nature. If the chain connects to an open edge of a graphene sheet (left hand side in Fig. 6a), the dangling bonds at the edge don't need to change their  $sp^2$  hybridized character when saturated with a chain. Electron transport over the contact can occur readily via the overlapping p-orbitals. A different situation appears when the chain bonds to a closed graphitic structure such as the end cap of a carbon nanotube (right hand side in Fig. 6a; this is an experimentally relevant situation, see Fig. 2b). A carbon atom of the tube wall changes its hybridization towards  $sp^3$  so that it can form four bonds and connects to the chain. However, this atom has no more extra p-electron so that a gap in the overlapping p-electrons appears at the contact and the electrical conductivity is impeded.

The type of bonding to contacts has an important influence on the modification of the chain. If we take a contact to an open graphene sheet, we may have two different situations. If the chain only forms one bond to the graphene edge (Fig. 6b), the next has to be a triple bond so that the structure of polyynes is imposed on the chain. If the first bond is a double bond, the only possible structure of the chain is cumulene (Fig. 6c). However, it has to be kept in mind that this picture is just an illustration and simplifies the situation. In reality, the electron distribution can be more or less uniform so that only a slight enhancement or lowering of the p-electron density over a certain bond occurs. The question is whether dimerization occurs, and this might even be the case when there is only a very slight non-uniformity in the electron distribution. It should also be noted that a polyyn chain with a single terminating bond to an end group needs an even number of atoms in the chain. Odd-numbered chains with a single end bond are in an electronically frustrated configuration.



**Fig. 6** **a** Local hybridization of carbon atoms at the end contacts of a carbon chain (courtesy of J.-C. Charlier). There is a continuous overlap of p-orbitals across the left hand side junction at the  $sp^2$  edge of graphene whereas the  $sp^3$ -hybridized carbon atom at the tube cap leaves a gap in the electron distribution. **b** and **c** show junctions between a graphene edge (blue) and a carbon chain (grey). If the chain is attached with a single bond, the structure of polyyn is imposed. Two bonds at the end impose the structure of polyyn throughout the chain.

The important mechanical properties of a carbon chain are the elastic modulus, the ultimate strain where fracture occurs and the fracture strength. The calculated elastic modulus is  $3 \times 10^{13}$  Pa which is extremely high, placing carbon chains among the stiffest known materials [13]. The ultimate strength is approximately 15%, making this stiff material surprisingly flexible. The fracture strength is predicted to be  $10^{-8}$  N for a single chain. Coming along with the extreme rigidity of carbon chains, the thermal conductivity by phonon propagation is also expected to be exceptionally high. The vibrational properties [5, 14] are governed by the strong covalent bonds and the extreme anisotropy. Vibration modes normal to the chain are much softer than in the direction of the chain.

### **Synthesis of $sp^1$ -carbon**

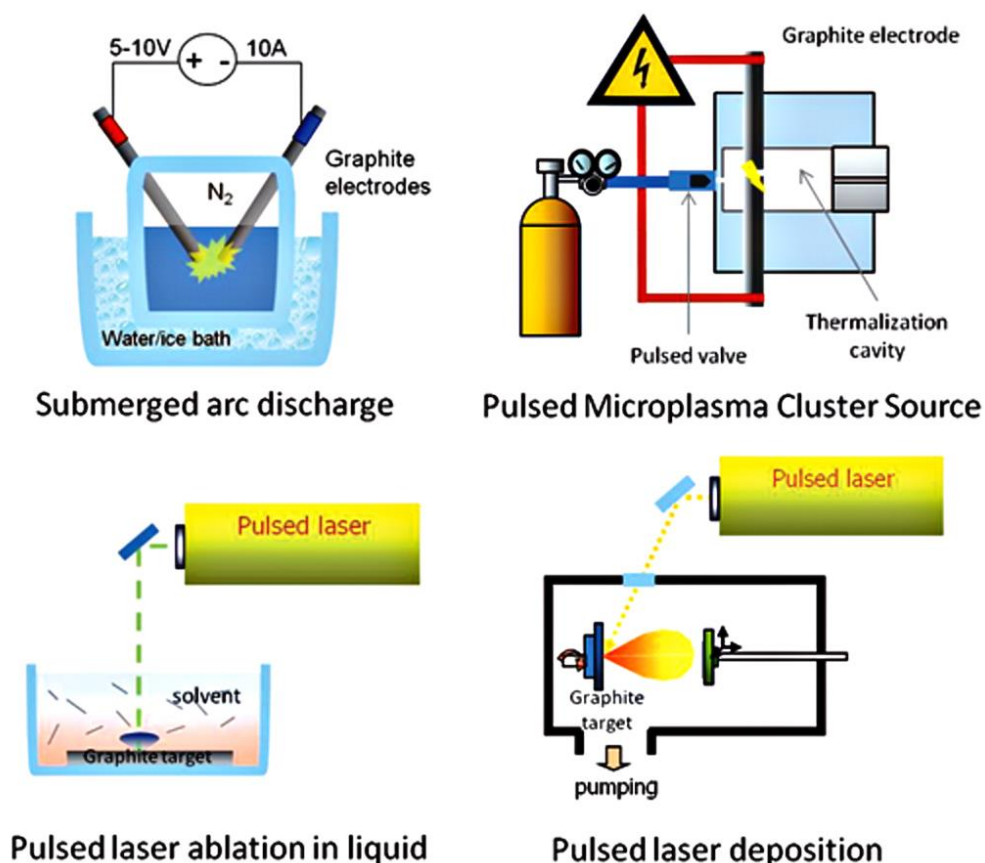
If we consider the synthesis of  $sp^1$  carbon, we have to distinguish between the generation of individual carbon chains and the synthesis of bulk carbyne. An important property of the chains is their high chemical reactivity and their instability against transformation to more stable  $sp^2$  carbon. Isolated chains of carbon atoms are only attached at their ends and therefore more stable than bulk phases because no reaction between different chains (cross-linking) is possible.

Several physical routes towards the generation of individual carbon chains have been studied. Electron microscopy has played an important role because the chains, once they have formed, can be immediately observed. Some simple but not very reliable techniques have been found. One possibility is the sputtering of carbon atoms from graphene or carbon nanotubes by the energetic electrons that are used for imaging in the electron microscope. Lateral thinning of a graphene layer can ultimately leave a chain [15, 16]. The same can be done by thinning a carbon nanotube until a chain is left between the separating ends (hour glass geometry) [17]. The chains can also be unraveled from graphene edges when a sharp tip (such as used in a tunneling microscope) is "welded" electrically to the graphene layer and then retracted. The latter technique allows studying the electrical properties of the chains immediately after their synthesis [10].

Bulk phases of carbyne have already been synthesized since decades [1, 2] but the characterization of the substance showed quite different appearances and properties. Generally, bulk carbyne is thought to be a macroscopic bundle of carbon chains where the individual strings are in an ordered lattice, but disordered arrangements could also be possible. It is undisputed that bulk carbyne is a metastable material and relaxes towards graphitic carbon by internal cross-linking of the chains. The relaxation is exothermic and might even be explosive [18]. Due to the fact that many studies of carbyne synthesis are not undisputed and there are even doubts about the

existence of stable bulk carbyne [19], the different approaches are not described in detail here but can be found in the literature [1, 2, 5, 20, 21].

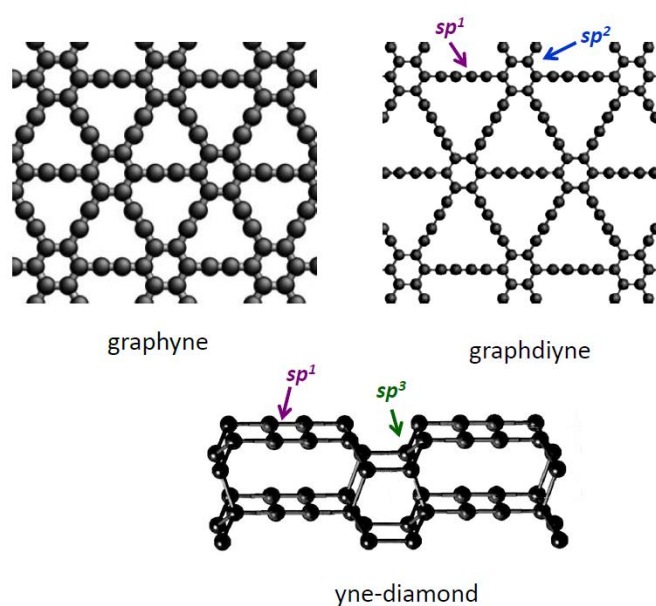
The synthesis has been carried out by chemical and physical approaches as shown in Figure 7. Several physical vapour deposition techniques have been reported such as the quenching of a plasma between carbon electrodes [22] or laser ablation of carbon [23]. However, these techniques mostly result in a mixture of  $sp^1$  and  $sp^2$  materials so that a separation of the phases, e.g., by chromatography has to follow. A quite spectacular study has been published recently [24] where a crystalline arrangement of carbon chains in a bulk material of white colour is synthesized by laser ablation in a liquid. However, the interpretation of the results of this study has been challenged [19]. The common ground of physical techniques is that the processes are far from thermal equilibrium and leave metastable structures that didn't have enough time to relax into the energy minimum. It is therefore assumed that carbon chains appear as transient states in very dynamic processes such as carbon evaporation at very high temperature and re-condensation. The experimental goal is to interrupt the reaction by rapid quenching before stable carbon phases have been reached.



**Fig. 7** Physical techniques for the synthesis of carbyne (courtesy C. Casari, reprinted with permission from Istituto Lombardo [25]).

Many attempts of chemical syntheses have been undertaken by polymerization. The polymerization of acetylene, where the two carbon atoms are already  $sp^1$ -hybridized ( $H-C\equiv C-H$ ) or the dimerization of ethynyl groups ( $H-C\equiv C-$ ) lead to bulk materials with  $sp^1$  bonds [26]. However, the material is polydisperse and not pure carbyne. Since the end atoms of the chains are very reactive, chemical approaches tend to stabilize the chains by end groups. Different end groups have been used, ranging from hydrogen or metal atoms to larger complexes. With larger end groups, chains of up to 44 atoms have been synthesized [27]. It is assumed that the extended end groups prevent cross-linking of the chains by keeping them at a distance. It is also important that bonding to the end groups has to be sufficiently strong, e.g., by aromatic species. Generally, polyynes are easier to synthesize, most likely due to their higher stability than cumulenes that relax more easily into graphitic or amorphous  $sp^2$  material. An overview of the many different routes of synthesis can be found in the literature [1, 2, 5, 20, 21].

Besides carbyne, which is (at least theoretically) a pure  $sp^1$  system, mixed carbon structures, where  $sp^1$  as well as  $sp^2$  or  $sp^3$  bonds occur, have also been studied [3]. Figure 8 shows some examples. Graphyne is a network of hexagons with internal  $sp^2$  bonds that are linked by shorter or longer  $sp^1$  chains [28]. Graphynes have already been synthesized and might be of interest for optoelectronic applications. A mixture of  $sp^1$  and  $sp^3$  bonds occurs in "yne-diamond" where unit cells of diamond are linked by carbon chains. This is predicted to be a superhard material but is still somewhat hypothetical. As another hybrid materials, carbon chains encapsulated in carbon nanotubes have already been synthesized and characterized by Raman spectroscopy and electron microscopy [29]. Here, van der Waals interaction stabilizes the atomic chains in the center of the nanotubes, avoids reactions with the end atoms and thus allows exceptionally long chains.



**Fig. 8** Possible carbon structures where the  $sp^1$  bond appears together with  $sp^2$  or  $sp^3$  bonds.

Once carbon chains or carbyne are synthesized, the material has to be characterized and identified as  $sp^1$  carbon. For individual chains, high-resolution microscopy techniques are necessary since macroscopic techniques (e.g., optical spectroscopy) do in most cases not provide enough signal from individual atomic species. Due to the high reactivity of the chains, deposition on a substrate is less favourable so that scanning tip microscopies (STM, AFM) can hardly be applied. However, by transmission electron microscopy, free-standing chains that are spanning between two contact points can be seen and characterized [9, 10, 15, 16, 17]. Carbyne as a bulk phase mostly consists of a mixture with other species so that signals from the particular bonding character of cumulene or polyynes have to be searched. This has been successful by Raman spectroscopy which shows the vibrational signatures of the different bonds [5, 14].

## Conclusions

We have now seen that carbon in the elemental  $sp^1$  hybridization has many facets of appearance. While we can even see individual carbon chains in microscopy pictures, the existence of a stable bulk phase of carbyne is still subject of controversial discussions. Experimental evidence has clearly shown that bulk phases of carbon containing a certain amount of  $sp^1$ -bonded atoms can be made; however, it seems rather unlikely that substantial quantities of pure bulk carbyne will ever be available as a standard material such as the more stable phases graphite or diamond. This is due to the high reactivity of the ends of carbon chains and the instability of neighbouring chains against cross-linking and successive relaxation towards  $sp^2$  carbon.

Individual carbon chains, on the other hand, are highly interesting species from a fundamental scientific point. They give us, for the first time, the possibility to study a perfectly one-dimensional electrical conductor. Similarly as graphene, they have a thickness of only one carbon atom and are as thin as a material ever can be. They are therefore the extreme case of a linear metal which Peierls already considered in the 1930s. Due to the high reactivity of the chains, their experimental handling remains difficult so that sophisticated experiments have to be designed to study their behaviour. Due to their atomic thickness, carbon chains would be the ultimate wire for interconnecting nanodevices but, again, their high reactivity makes such a possible application highly speculative. Nevertheless, understanding their structure and properties allows us to gain fundamental insight into the principles of one-dimensional atomic structures.

## Acknowledgements

The author wishes to thank his former PhD students and postdocs O. Cretu, A. La Torre and F. Ben Romdhane for several years of excellent work on carbon chains. He is also grateful to J.-C. Charlier, A. Botello-Mendez and J.-J. Adjizian for fruitful collaboration. Financial support from the LABEX program “Nanostructures in Interaction with their Environment”, project ANR-11-LABX-0058 NIE has made the work on carbon chains possible.

## References

1. Heimann RB, Evsyukov SE, Kavan L (1999) *Carbyne and Carbynoid Structures*. Kluwer Acad. Publ., Dordrecht
2. Cataldo F (2005) *Polyynes: Synthesis, Properties, and Applications*. CRC Press, London
3. Hirsch A (2010) *Nature Mater* 9:868-871
4. Banhart F (2015) *Beilstein J Nanotechnol* 6:559-569
5. Casari CS, Tommasini M, Tykwinski RR, Milani A (2016) *Nanoscale* 8:4414-4435
6. Ohnishi H, Kondo Y, Takayanagi K (1998) *Nature* 395:780–783
7. Peierls RE (1964) *Quantum Theory of Solids*. Clarendon, Oxford
8. Artyukhov VI, Liu M, Yakobson BI (2014) *Nano Lett* 14:4224–4229
9. Lin YC, Morishita S, Koshino M, Yeh CH, Teng PY, Chiu PW, Sawada H, Suenaga K (2017) *Nano Lett* 17:494–500
10. Cretu O, Botello-Mendez AR, Janowska I, Pham-Huu C, Charlier JC, Banhart F (2013) *Nano Lett* 13:3487–3493
11. La Torre A, Botello-Mendez A, Baaziz W, Charlier JC, Banhart F (2015) *Nature Comm* 6:6636
12. Ben Romdhane F, Adjizian JJ, Charlier JC, Banhart F (2017) *Carbon* 122:92-97
13. Liu M, Artyukhov VI, Lee H, Xu F, Yakobson BI (2013) *ACS Nano* 7: 10075–10082
14. Milani A, Tommasini M, Russo V, Li Bassi A, Lucotti A, Cataldo F, Casari CS (2015) *Beilstein J Nanotechnol* 6:480–491
15. Chuvilin A, Meyer JC, Algara-Siller G, Kaiser U (2009) *New J Phys* 11:083019
16. Jin C, Lan H, Peng L, Suenaga K, Iijima S (2009) *Phys Rev Lett* 102:205501
17. Troiani HE, Miki-Yoshida M, Camacho-Bragado GA, Marques MAL, Rubio A, Ascencio JA, Jose-Yacamán M (2003) *Nano Lett* 3:751–755
18. Baughman RH (2006) *Science* 312:1009–1010
19. Tarakeshwar P, Buseck PR, Kroto HW (2016) *J Phys Chem Lett* 7:1675-1681
20. Szafert S, Gladysz JA (2003) *Chem Rev* 103:4175-4206
21. Januszewski JA, Tykwinski RR (2014) *Chem Soc Rev* 43:3184-3203
22. Cataldo F (2003) *Carbon* 41:2671-2674



23. Hu A, Lu QB, Duley WW, Rybatchuk M (2007) *J Chem Phys* 126:154705
24. Pan B, Xiao J, Li J, Liu P, Wang C, Yang G (2015) *Sci Adv* 1:e1500857
25. Casari CS (2012) *Istituto Lombardo (Rend. Scienze)* 146:17-35
26. Siemsen P, Livingston RC, Diederich F (2000) *Angew Chemie Int Ed* 4:2632-2657
27. Chalifoux WA, Tykwinski RR (2010) *Nature Chem* 2:967–971
28. Ivanovskii AL (2013) *Prog Solid State Chem* 41:1-19
29. Shi L, Rohringer P, Suenaga K, Niimi Y, Kotakoski J, Meyer JC, Peterlik H, Wanko M, Cahangirov S, Rubio A, Lapin ZJ, Novotny L, Ayala P, Pichler T (2016) *Nat Materials* 15:634-639