Are we approaching close to sp-hybridized carbon allotrope?

C. Srinivasan and R. Saraswathi

It is astonishing that nature has chosen the element carbon as the basis of life. One reason that scientists attribute to this choice is the exceptionally strong bond between carbon atoms and indeed we are aware that one form of carbon, diamond, has emerged as the strongest material. For a long time only two bulky forms of carbon, viz. diamond and graphite were known as its allotropes. Although the bonds between carbon atoms are characterized by sp^3-hybridization in diamond, sp^2-hybridized carbon atoms are involved in bond formation in graphite. Buckminsterfullerene (C_{60}), the third form of carbon, was first reported in 1985 by Kroto *et al.*[1]. C_{60} has several unique distinctions – it is the only allotrope of an element to be discovered in the 20th century and fullerenes have the maximum number of atoms in a molecule of the same element. Another notable advancement in the study of various forms of carbon is the serendipitous observation by Iijima[2] of needle-like materials in the carbon cathode employed in the arc-discharge process for the synthesis of fullerenes that led to the discovery of carbon nanotubes, the name proposed for ultra-thin carbon fibre with nanometre-size diameter and micrometre length. The originally obtained by-product in the synthesis of C_{60} was only multi-walled carbon nanotubes. The synthesis of single-walled carbon nanotubes having diameters varying from 1 to 3 nm and length of 100 μm followed soon[3,4]. With the advent of sp^2-hybridized carbon nanomaterials, it is not surprising to expect the sp-carbon allotrope, carbyne, having an one-dimensional, rod-like structure made of infinite number of alternating single and triple bonds (Figure 1 *a*). Fortuitous it may be, to observe a striking but strange coincidence in the history of discovery of fullerenes and carbyne. While Kroto strongly believed in the presence of different forms of carbon in interstellar dust thus laying the base for the discovery of fullerenes, others proposed the existence of carbyne in interstellar dust[5], meteorites[6] and as a by-product of shock-fused graphite[7].

The unabated interest in carbon nanostructures has stemmed from their unprecedented properties, and the availability of more sophisticated methods for characterization has stimulated the vigour for the synthesis of this linear, one-dimensional framework of carbon. In this context, intensive efforts were initiated to synthesize polyynes, which are considered as low molecular weight oligomeric model compounds for carbyne.
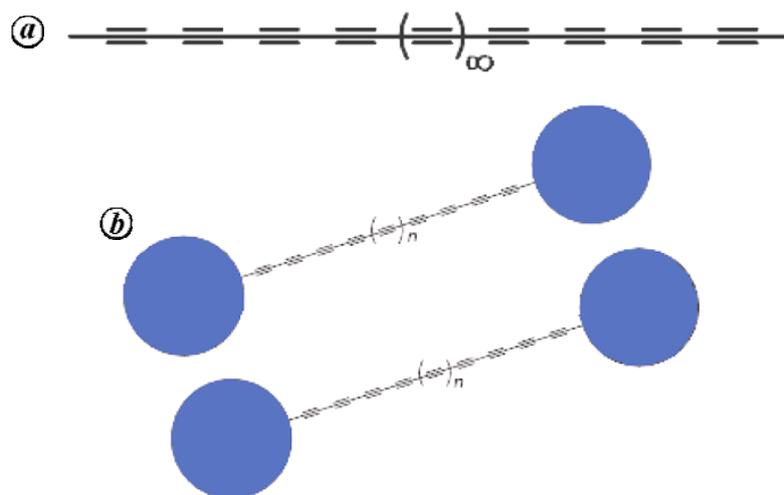
Figure 1. *a*, The sp-carbon allotrope carbyne. *b*, Dumb-bell shaped polyynes with sterically demanding end-caps preventing cross-linking.
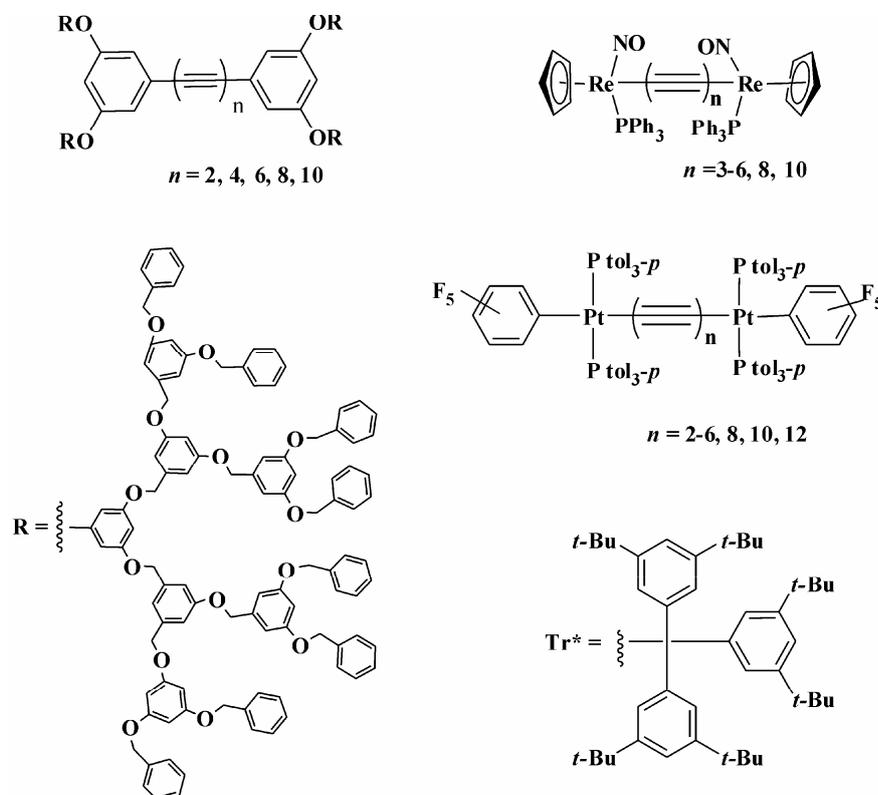
Figure 2. Some end-capped polyynes. *n* represents the number of triple bonds. The structure of the capping group Tr* is also shown.
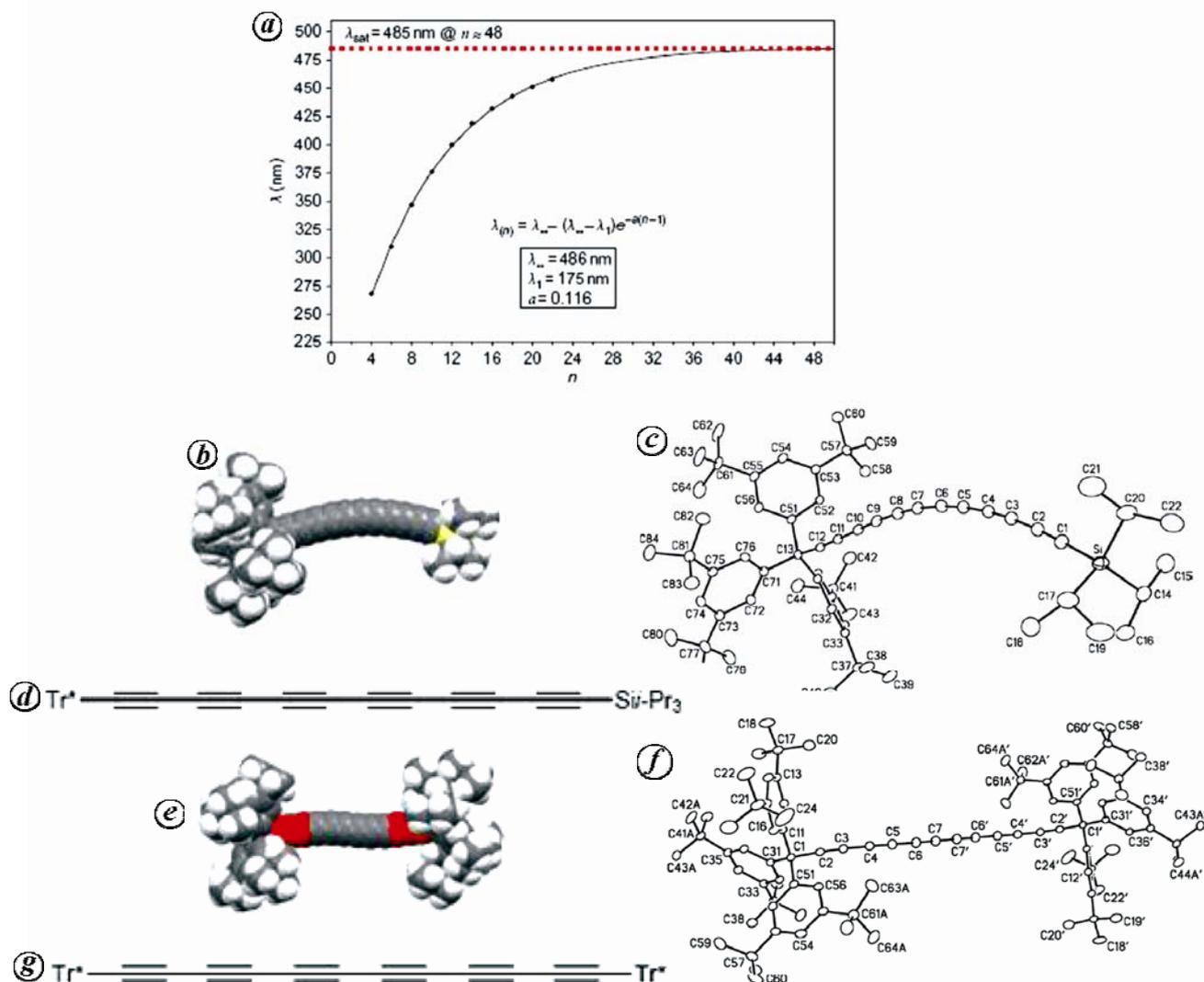
Figure 3. *a*, Convergence of the absorption maxima in the series of polyynes. Crystallographic characterization of the hexaynes. (*c*) and (*f*). X-ray crystallographic structures for *c* and *f* shown as space-filling models (*b* and *e*) and ORTEP representations (right, 20% probability level, hydrogen atoms not shown); selected bond lengths (Å) for (*c*) C(1)–C(2) 1.213(3), C(2)–C(3) 1.357(4), C(3)–C(4) 1.209(3), C(4)–C(5) 1.360(4), C(5)–C(6) 1.211(3), C(6)–C(7) 1.358(3), C(7)–C(8) 1.202(3), C(8)–C(9) 1.360(4), C(9)–C(10) 1.210(3), C(10)–C(11) 1.364(3), C(11)–C(12) 1.196(3); selected bond lengths (Å) for (*f*) C(2)–C(3) 1.192(3), C(3)–C(4) 1.363(3), C(4)–C(5) 1.205(3), C(5)–C(6) 1.353(3), C(6)–C(7) 1.201(3), C(7)–C(7′) 1.362(5). (Reproduced from Chalifoux and Tykwinski[12] with permission from Nature Publishing Group.)

Cataldo[8] proposed a method in solution and concluded that at relatively high concentration ($>10^{-3}$ M) in solution and in the solid state the polyynes were unstable and gave a brown precipitate resembling cork. This solid is suggested to be a polyaddition product of the polyynes, although there is evidence for oxidation[8] and thus the parent allotrope itself is still elusive. Since the attempted synthesis of carbyne resulted in ill-defined products, many believed that capping the two ends of the linear polymer with bulky groups would provide stability. In recent years a number of

model compounds with end-capped polyynes (oligomers) have been synthesized and characterized. Incorporation of bulky groups as capping moieties at both ends of the polyynes like a dumb-bell (Figure 1 *b*) prevents unwanted side reactions and polymerization. The capping groups provide stability to the polyynes by preventing unwanted reactions through steric and/or electronic effects. The synthesis of decayne containing ten triple bonds which span two redox-active, chiral rhenium fragments has been reported[9]. This polyyne is also stable at room temperature. Gibtner *et al.*[10]

described in detail the synthesis of three series of differently 3,5-disubstituted α,ω-diphenylpolyynes, Ar–(C≡C)$_n$–Ar (n = 2, 4, 6, 8, 10).

Some groups employed as end-capping agents[11] are shown in Figure 2. In addition, triisopropylsilyl groups (TIPS) and quite recently, tris(3,5-di-*tert*-butyl-phenylmethyl) moiety[12] (Tr*) (Figure 2) have been employed as end-capping agents. Since Tr* is a large, sterically demanding end-group, Chalifoux and Tykwinski[12] concluded that synthesis of much longer polyynes will be feasible. Recently, they reported the synthesis of

polyynes with 4, 6, 8, 10, 12, 14, 16, 18, 20 and 22 triple bonds. The significant outcome of the study is that the step-wise synthetic procedure developed for such polyynes can be scaled up to make higher polyynes and even carbyne.

These polyynes are not particularly sensitive to light, moisture or oxygen, and they can be handled and characterized under normal laboratory conditions. Their X-ray crystallographic analysis, ^{13}C NMR and UV–visible spectral studies shed much light on their properties.

It is evident from X-ray crystallographic analysis that the structure shown in Figure 3 d (containing Tr* and TIPS as end-capping moieties) is slightly bent and that of Figure 3 g (with Tr* as end-capping groups) is almost linear (see also the corresponding space-filling model and ORTEP representations in Figure 3). These observations reveal that the Tr* group extends well outside the sp-carbon framework and offers significantly more steric shielding against unwanted inter-molecular interactions that reportedly lead to decomposition (schematically shown in red in Figure 3 b and e)[12]. The bond lengths disclose the presence of alternating carbon–carbon single and triple bonds.

^{13}C NMR spectra of the synthesized polyynes provide ample evidence for the presence of sp-hybridized carbon. For the longest polyyne with 22 triple bonds,

21 NMR signals are discernable (two overlapping signals are observed at 64.27 ppm). The signals appear in the narrow range of 62.10–64.60 ppm, with a median value of 63.7 ppm, except for the two end carbons attached to Tr*.

As expected, in the UV–visible spectrum of the polyynes, the lowest energy band experiences a bathochromic shift with increasing length. This causes lowering of the energy between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). A plot of λ_{max} values of the polyynes versus n (the number of triple bonds) reveals a convergence limit (Figure 3 a). From the convergence limit of λ_{max}, it has been estimated that the HOMO–LUMO energy gap for carbyne is 2.54 eV.

Thus the search for new molecular and regular polymeric allotropes of carbon has stimulated the preparation and study of π-conjugated acetylenic macrocycles, which are likely to exhibit exciting properties like the other carbon nanomaterials.

1. Kroto, H. W., Heath, J. R., O'Brien, S., Curl, R. F. and Smalley, R. F., *Nature*, 1985, **318**, 162–163.
2. Iijima, S., *Nature*, 1991, **354**, 56–58.
3. Iijima, S. and Ichihashi, T., *Nature*, 1993, **363**, 603–605.
4. Bethune, D. S., Kiang, C. H., de Vries, M. S., Gorman, G., Savoy, R. and Bevers, R., *Nature*, 1993, **363**, 605–607.
5. Webster, A., *Mon. Not. R. Astron. Soc.*, 1980, **192**, 7–9.
6. Hayatsu, R., Scott, R. G., Studier, M. H., Lewis, R. S. and Anders, E., *Science*, 1980, **209**, 1515–1518.
7. El Goresy, A. and Donnay, G., *Science*, 1968, **161**, 363–364.
8. Cataldo, F., *Carbon*, 2005, **43**, 2792–2800.
9. Brady, M., Weng, W. and Gladysz, I. A., *J. Chem. Soc. Chem. Commun.*, 1994, 2655–2657; Bartik, T., Bartik, B., Brady, M., Dembinski, R. and Gladysz, J. A., *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 414–417; Dembinski, R., Bartik, T., Bartik, B., Jaeger, M. and Gladysz, J., *J. Am. Chem. Soc.*, 2000, **122**, 810–822.
10. Gibtner, T., Hampel, F., Gisselbrecht, J.-P. and Hirsch, A., *Chem. Eur. J.*, 2002, **8**, 408–432.
11. Eisler, S., Aaron, S. E., Slepkov, D., Elliott, E., Luu, T., McDonald, R., Hegmann, F. A. and Tykwinski, R. R., *J. Am. Chem. Soc.*, 2005, **127**, 2666–2676.
12. Chalifoux, W. A. and Tykwinski, R. R., *Nature Chem.*, 2010, **2**, 967–971.

C. Srinivasan* lives at 1, Subash Street, Kalvinagar, Theni Main Road, Nagamalai, Madurai 625 019, India; R. Saraswathi is in the Department of Materials Science, Madurai Kamaraj University, Madurai 625 021, India.
*e-mail: ceesri@yahoo.com

Wheat genome sequence: challenges and success

Satish Kumar, Chandan Kumar Singh and Rajib Bandopadhyay

Wheat is one of the most important staple food crops of the world, occupying 17% (one-sixth) of crop acreage worldwide, feeding about 40% (nearly half) of the world population and providing 20% (one-fifth) of total food calories and protein in human nutrition[1]. Global wheat production has been under threat in recent years from increasing demand and climate change. China, the world's largest wheat producer and consumer, is facing its own grain security problem and is eager to increase crop yields amid shrinking farmland and a rising population. Recently, Russia, one of the biggest

producers of wheat, banned all export of wheat after severe drought and wildfire charred crops around the country. Major floods in Pakistan and mudslides in China made wheat prices go up even further. Canada and several other countries also expect their wheat harvest to be much lower compared to the previous year due to weather conditions. The move raised worldwide concerns about possible wheat shortages and has sent wheat prices soaring. Sequencing the wheat genome could help identify and manipulate specific genes for useful traits, such as tolerance to drought, resis-

tance to crop diseases, or better grain quality. We can expect that improved crop management will provide at least 50% of the solution. Further, because of its recent history, hexaploid wheat is a good model to study polyploidy, a driving force for plant genome evolution.

Wheat is adapted to temperate regions of the world and was one of the first crops to be domesticated some 10,000 years ago. At the cytogenetic level, common wheat is known to have three sub-genomes (each sub-genome has seven chromosomes, making $n = 21$) that are organized in seven homoeologous