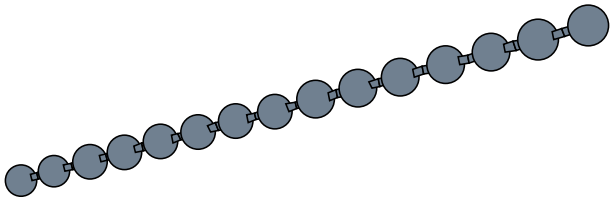
Gaining knowledge of single carbon chains

J.P. Boersma, JP.Boersma@science.ru.nl

With thanks to:
Mikhail Akhukov, Annalisa Fasolino
Theory of condensed matter, Radboud University Nijmegen

June 29, 2011



Contents

1

Abstract

There is not much knowledge of the behavior of nanosized parts of graphene. One interesting question is whether carbon ribbons or chains could be used to connect graphene parts and serve as a current conductor. Therefore we did calculations on 'single' graphene ribbons (benzene stripes) at first, which point out that the stripes aren't stable. Two periodic chains are formed. Instead of periodic chains we did mostly calculations on finite carbon chains, which are more relevant for our question. Previous research has shown that these chains are stable [1]. We studied the convergence of energies, distances and distance alternation in chains with periodic and free boundary conditions and in carbon chains with varying termination. These terminations were one, two or three hydrogens or a graphene ribbon. The bond lenghts, binding energies and charge densities were determined for these chains. From these properties we can conclude that adding termination to isolated carbon chains causes more alternation in bond lengths. There is a difference in formation energies and bond lengths between an even and odd number of carbon atoms in a chain and thus a difference in stability with the chain with an even number of carbon atoms being the stablest chain.

2

Introduction

Knowledge and research about the structure of graphene has opened new doors to carbon based electronics [7] and many other fields. The importance of the discovery of graphene has been confirmed by the physics Nobel prize award in October 2010, awarded to Andre Geim and Konstantin Novoselov.

A one-dimensional graphene sheet is equal to a single carbon chain. This is the smallest possible part of graphene. Knowledge is needed of these carbon chains since this is the base of graphene. Carbon chains have also been found in space. Information about these chains may be valuable for astrophysics [8, 9].

The bond lengths of carbon chains characterizes the type of bond between the carbons, for example alkanes have a bond length of 1.53 Å , alkenes 1.33 Å and alkynes 1.20 Å [10] .

In chemistry, two useful types of carbon chain structures are cumulenes and polyynes. Cumulene type carbon chains have consecutively two or more 'double bond' type bond lengths and are conductors [6]. Polyyne type carbon chains have alternating single and triple bond lengths and are insulators. By looking at the distances in the carbon chains the type of chain can be determined.

3

Computational Methods

A series of density functional theory (DFT) calculations based on localized orbitals were performed within the SIESTA program [2]. We used general gradient approximation with Perdew–Burke–Ernzerhof parametrization (PBE-GGA) [3]. A standard built-in double-ζ polarized (DZP) [4] basis set was used for all calculations. The cutoff radii of the atomic orbitals were obtained from an energy shift equal to 1.0 mRy. The real-space grid is equivalent to a plane wave cutoff energy of 360 Ry. For all non periodical directions an extra space larger than 15 Å was added to avoid spurious interactions. Every geometry was relaxed using the conjugate gradient method (CG) until all forces were smaller than 0.04 eV/Å (6.409^{-11} N). After the SIESTA calculations the results were post-processed with the denchar program to calculate the charge densities.

4

Results & Discussion

4.1 Periodic & isolated carbon chains

In figure 4.1 the binding energies per atom of the periodic and isolated carbon chains are shown as a function of the number of carbon atoms in the chain. The binding energies of periodic chains are nearly constant but with a small alternation of 0.05 eV, whereas the binding energies of isolated chains are clearly increasing with the number of carbon atoms in the chain. The binding energies converge to -6.5 eV which is lower than the -6.73 eV of periodic chains. This difference is a result of the two edge atoms of the isolated chain.

The bond lengths of the periodic carbon chains are all 1.311 Å not depending on the length of the chain but slightly larger than the by Junquera et al. reported value, 1.28 Å [4]. This may be due to different settings for the calculations. We compared isolated carbon chains with an even and an odd number of carbon atoms. Therefore we looked at carbon chains with ten and eleven carbon atoms as an example of respectively even and odd. The bond lengths of these isolated carbon chains are shown in figure 4.2. We see a clear alternating behaviour in the bond lengths.

The charge densities of these two chains, shown in figures 4.3 and 4.4, confirm the alternating bond lengths of the isolated chains and the constant bond lengths of the periodic chains. The periodic chain has all similar charge densities around the atoms, the isolated chain has an alternating pattern in the densities. With figure 4.5 we can compare the charge densities of the isolated carbon chains with respectively ten and eleven carbon atoms. The densities look very similar, but are shifted compared to each other.

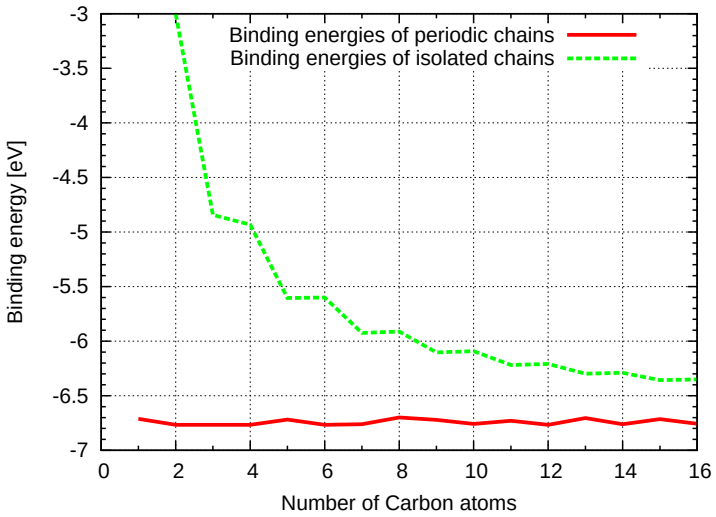


Figure 4.1: Binding energies of periodic and isolated carbon chains.

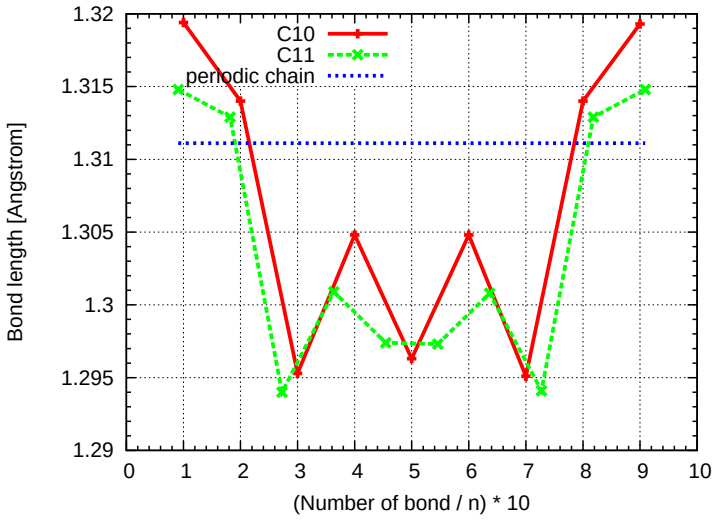


Figure 4.2: Bond lengths of isolated carbon chains with 10 and 11 carbon atoms.

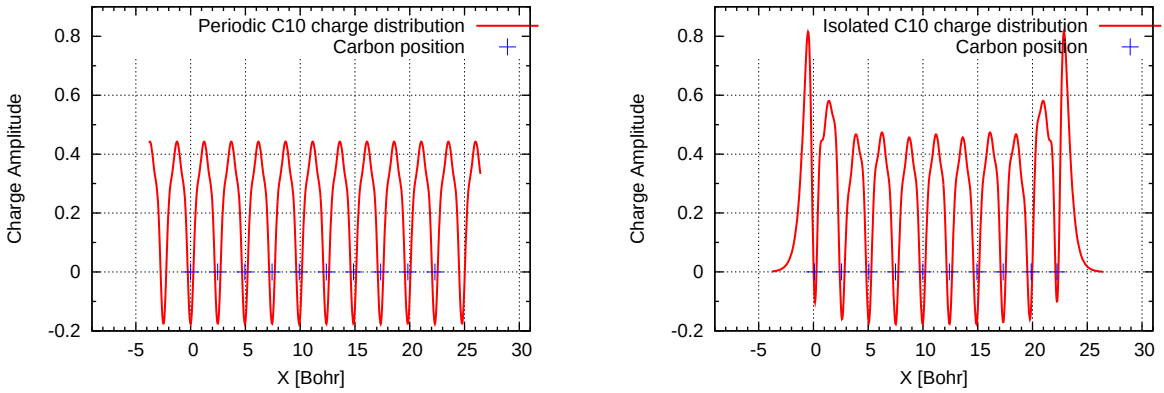


Figure 4.3: The charge densities of periodic (left) and isolated (right) chain with ten carbon atoms.

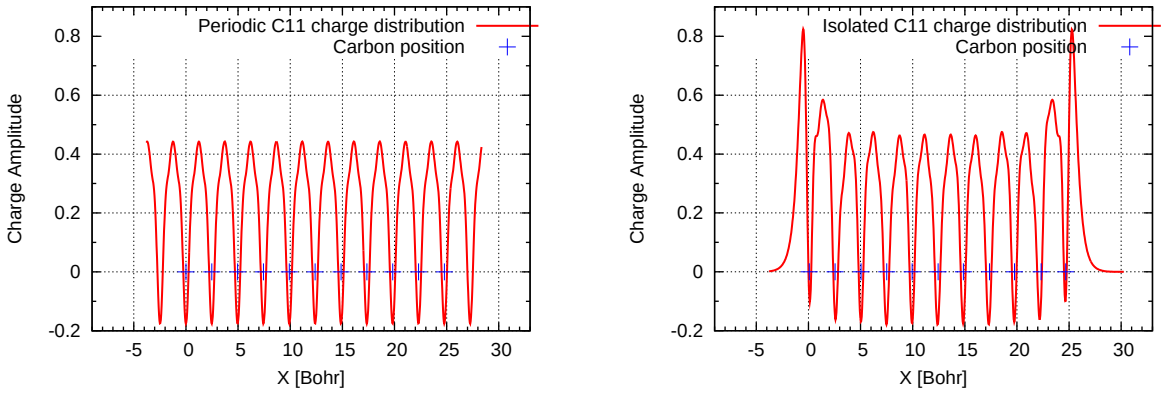


Figure 4.4: The charge densities of periodic (left) and isolated (right) chain with eleven carbon atoms.

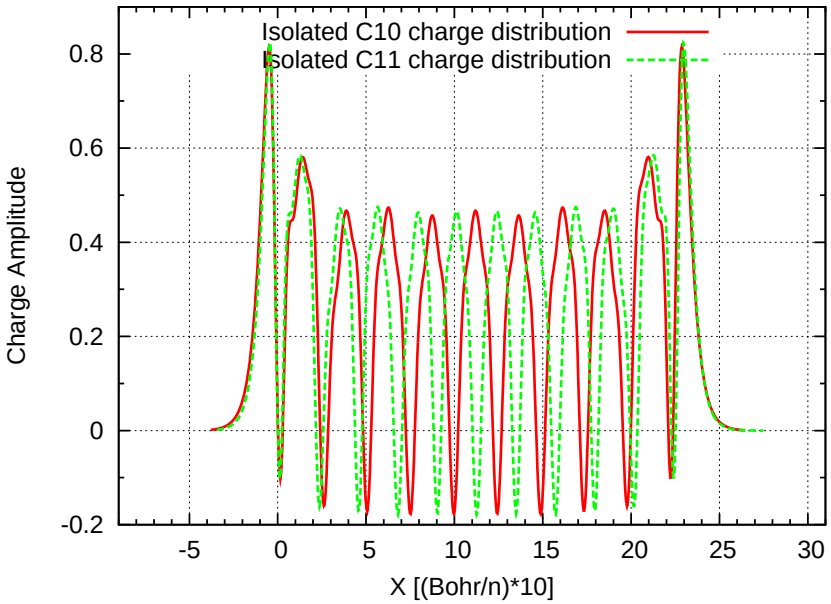


Figure 4.5: The charge densities of the isolated chain with ten and eleven carbon atoms.

4.2 Periodic carbon chain with ribbon

Figure 4.6 shows the carbon chain, made of six carbon atoms, connected to a graphene ribbon with periodic boundary conditions in the x- and y-direction. After minimization of energy the structure remains flat as shown in the figure. The bond lengths of the ribbon are around 1.41 Å on the outer bonds and 1.44 Å on the inner bonds.

The bond lenghts of the chain are shown in figure 4.7. Here we see a clearly larger (and shifted) alternation than the isolated carbon chain without termination. We also see an increased bond length in the bond between the chain and the ribbon.

Due to lack of resources, there could not be made any more calculations on this system. Therefore this system has been simplified: instead of ribbons, hydrogens were attached to the carbon chains.

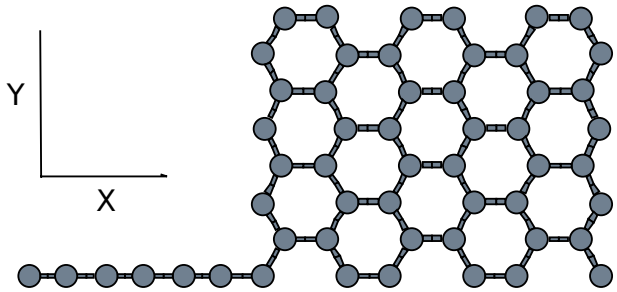


Figure 4.6: The calculated chain with ribbon.

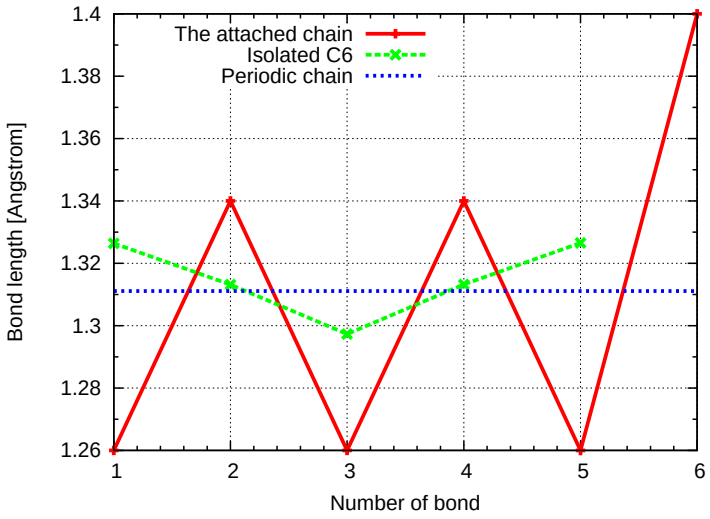


Figure 4.7: Bond lengths in the chain attached to the ribbon.

4.3 Isolated carbon chains with hydrogens

With a hydrogen termination, calculations were done on chains from two to sixteen carbon atoms with on both sides one, two or three hydrogen atoms. The hydrogens are placed like they are positioned in nature: the most stable position. For example the chain with on both sides three hydrogens is most stable in the staggered conformation (figure 4.8). Notice that we did research only on carbon chains with on both sides the same number of hydrogen atoms.

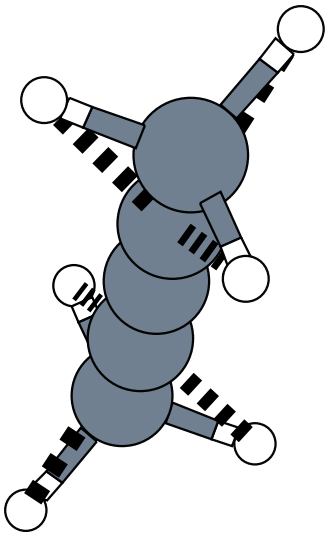


Figure 4.8: The staggered conformation of the chain with three hydrogen atoms on both sides.

Figures 4.9 and 4.10 show the bond lenghts of these chains with ten and eleven carbon atoms. From these figures we see that by adding hydrogens to the chain the alternation is changed. The chains with two and six hydrogens have a larger alternation with an amplitude of 0.1 Å . Interesting is, the chains with on both sides two hydrogen termination do not have much alternation at all. This may be because of the two hydrogen termination is bulk like. Therefore these chains act as cumulenes, while the one and three hydrogen terminated chains act as polyynes [6].

The bond lengths of the hydrogen terminated chains show an alternating pattern for both even and odd chains. For even chains the amplitude of alternation is constant. This in contrast to the odd chains, where the amplitude of alternation differs. In the middle of the odd carbon chain (the bond between carbon number 5 and 6) the bond lengths converge. This behaviour can be described as locally cumulene type [6]. In addition in 4.10 we see that the middle bond length of the carbon chain with eleven carbon atoms and six hydrogen termination is similar to those of the periodic chains.

From the above results we can conclude that even chains are polyyne like because the bonds between the carbons are in the order of triple-double, 1.25 Å - 1.35 Å . The literature claims that this is triple-single [5], 1.20 Å - 1.45 Å . This can be explained by a phenomenon called bond-flipping. The bonds flip between triple to double and single to double bonds and vice versa. Therefore the calculated distances are averages of these different bond lengths. This bond-flipping may have an effect on the conductivity of the chains, because these chains might not be totally polyyne type. In principle the chains with an odd number of carbon atoms are polyyne like, but as said earlier they seem to converge in the middle to cumulene (bulk) type. This too may have an effect on the conductivity of these chains, because this chain is not totally polyyne type.

Figure 4.11 shows the formation energies for an isolated chain, and chains with two, four or six hydrogens.

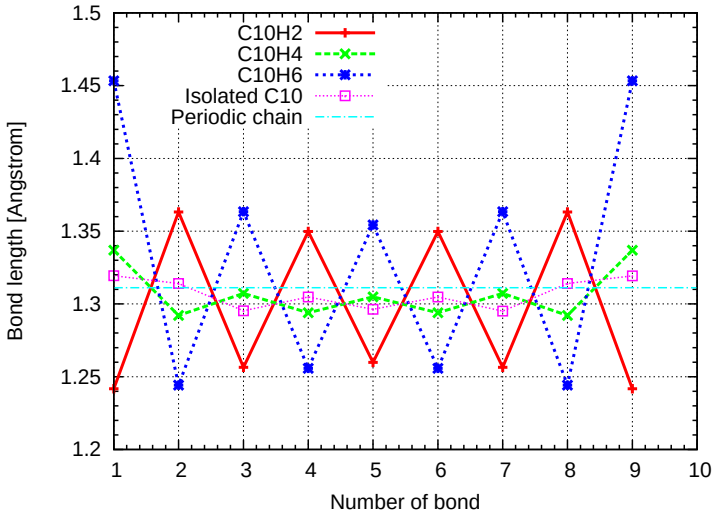


Figure 4.9: The distances of a chain with ten carbon atoms with a two, four and six hydrogen termination.

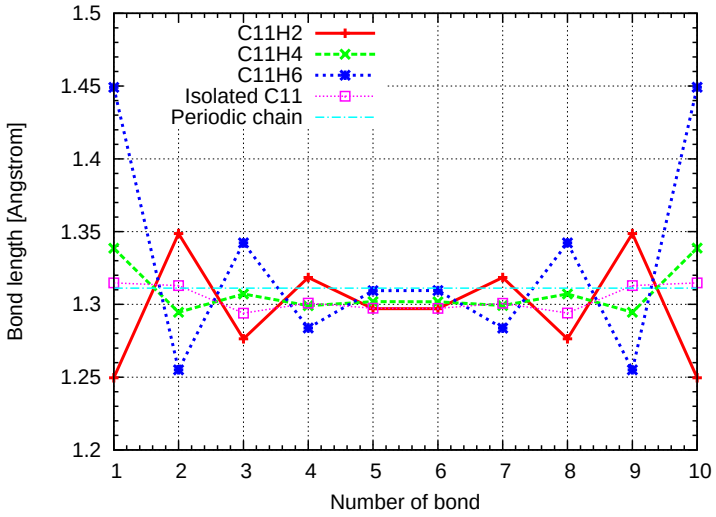


Figure 4.10: The distances of a chain with eleven carbon atoms with a two, four and six hydrogen termination.

The formation energies have been calculated with the formula

$$E_a = E_{tot}(C_a) – E_{tot}(C_{(a-1)}) – E_{tot}(C)$$

Where E_a is the formation energy of atom a , $E_{tot}(C_a)$ the total energy of a chain with a carbon atoms, $E_{tot}(C_{(a-1)})$ the total energy of a chain with $a-1$ atoms and $E_{tot}(C)$ the total energy of a carbon atom.

The formation energies show a clear alternating effect, which seems to converge around -6.8 eV.

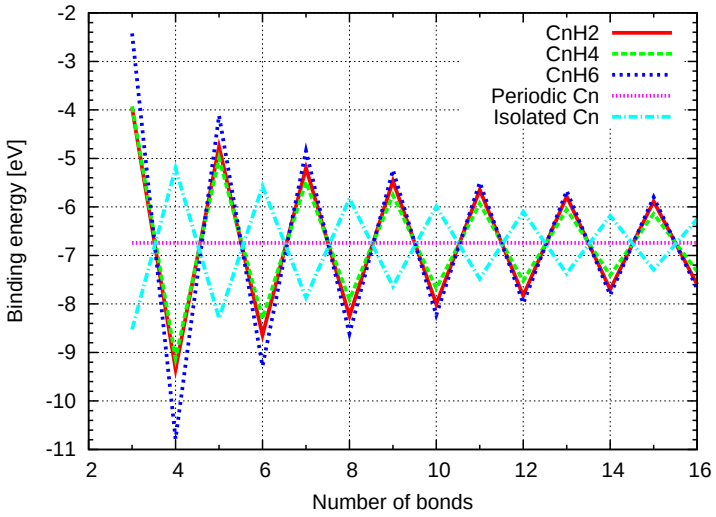


Figure 4.11: Formation energies of chains with two, four and six hydrogen atoms as termination and without termination.

However, there were also some differences found between an even and an odd number of carbon atoms. Both chains have negative binding energies, but the binding energy of a chain with an even number of carbon atoms is more negative than an odd chain. Thus an even chain will be more stable than an odd chain.

From this figure we can also see that adding carbon atoms to a hydrogen terminated even chain is energetically favourable. In contrast to even isolated chains (without termination), where adding carbon atoms is unfavourable. There is something interesting if we look at the rest of the trend: chains with two hydrogens show higher values than four hydrogens, and lower values than six hydrogens. This fits into the idea that the chains with two hydrogen termination are bulk like. When we look at the formation energy per atom we see that it is around 5.2 eV/Å .

In figure 4.12 we show the charge densities of the carbon chains with ten and eleven carbon atoms and two, four and six hydrogen atoms. The charge densities confirm what the bond lengths already concluded. The chains with two and six hydrogens have a large alternation, but the chains with four hydrogens have almost no alternation. The chains with an odd number of carbon atoms have no alternation in the middle of the chain.

In figure 4.13 the formation energy per hydrogen for a chain with ten carbon atoms is shown. Notice that the hydrogens are attached in pairs, one on both sides. A similar plot is found for a chain with eleven carbons. From this figure we can see that binding of the first pair of hydrogen atoms costs more energy than binding the second and the third pair of hydrogens. These results are incomplete because these calculations were only done for pairs of hydrogens, not individually.

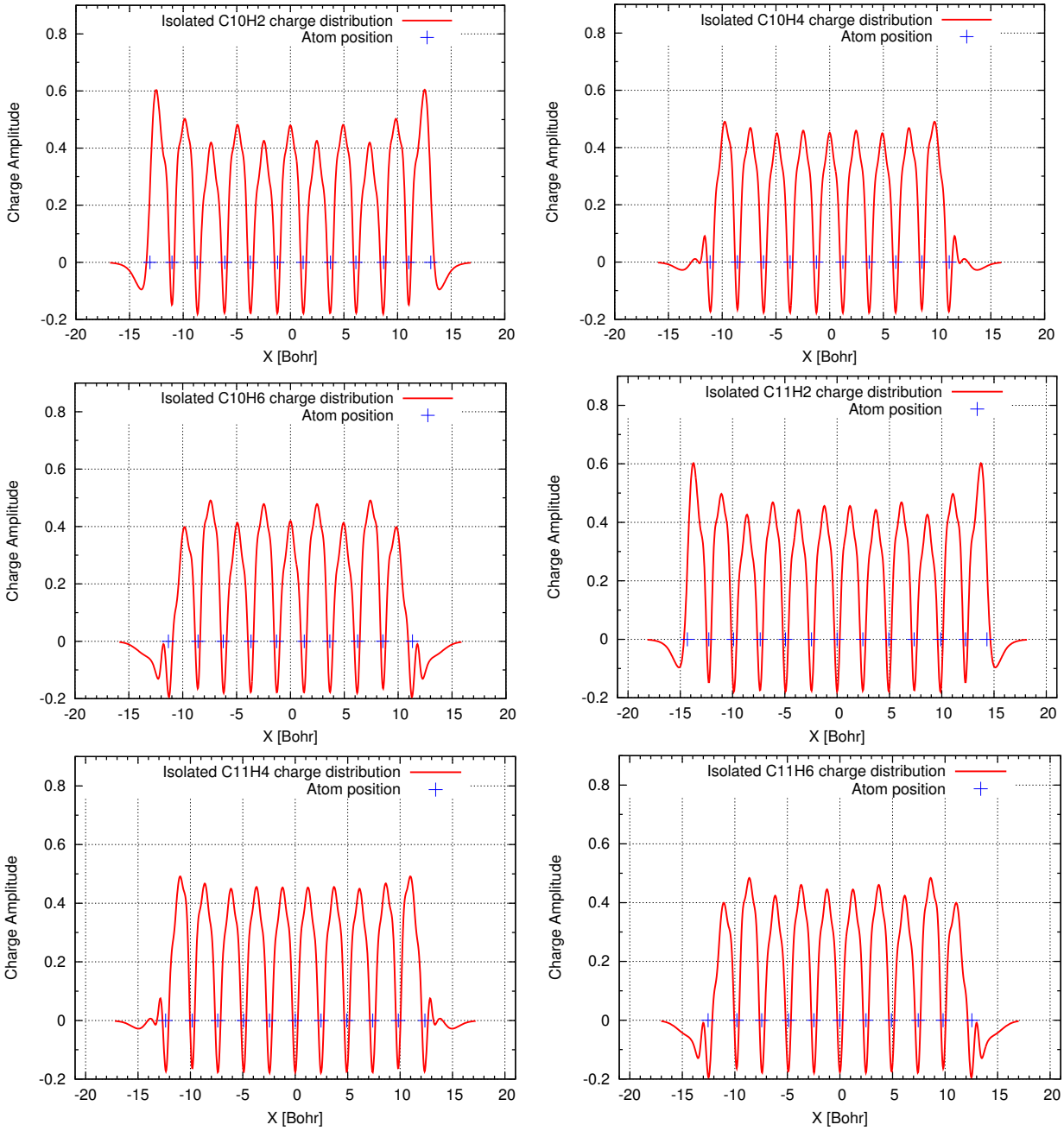


Figure 4.12: The charge densities of chains with ten and eleven carbon atoms with two, four and six hydrogen atoms attached.

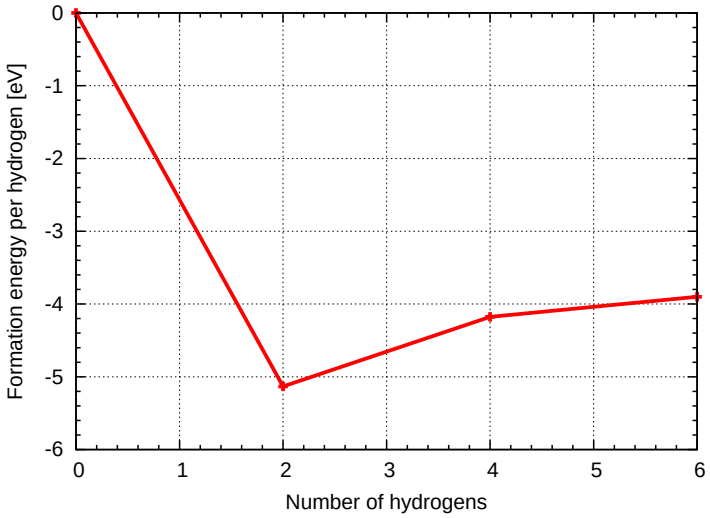


Figure 4.13: Formation energies per attached hydrogen atom.

5

Conclusion

The polyyne type bond lengths are found to be triple - double bonds instead of triple - single bonds, where the conductivity of the chain may have changed. Adding termination to isolated carbon chains causes a larger amplitude alternation in the bond lengths, and more termination causes more alternation. There is a difference in formation energies and bond lengths between an odd and even number of carbon atoms in a chain.

6

Future Plans

It may be interesting to see what carbon rings do when they get larger and larger. For example to see what kind of angles the C - C bonds have versus the number of carbon atoms in the ring. It is also better to do more calculations on the termination of the carbon chain and attach other atoms or molecules as termination, most importantly the graphene-like ribbon. In this case one needs a lot of computing power. The calculations on the hydrogen termination were done with two hydrogens at a time. It can be interesting to see odd numbers of hydrogens too. This way we can calculate the formation energy per hydrogen.

Lastly it may also be nice to do actual research on conductivity of the chains. Literature [6] tells us that cumulene type chains theoretical are conductive and polyynes are insulators and we found results where it may have some kind of hybrid structure.

References

[1] A. Chuvilin, J.C.Meyer, G. Algara-Siller, U. Kaiser, From graphene constrictions to single carbon chains. New J. Phys.: Vol. 11, (2009)

[2] J.M. Soler, E. Artacho, J.D. Gale, A. Garcia, J. Junquera, P. Ordejon, D. Sanchez-Portal, J. Phys.: Condens. Matter 14, 2745-2779 (2002)

[3] J.P. Perdew, K. Burke, M. Ernzerhof, Generalized Gradient Approximation Made Simple. Phys. Rev. Lett. 1996, 77, 3865.

[4] J. Junquera, O. Paz, D. Sanchez-Portal, E. Artacho, Numerical Atomic Orbitals for Linear-Scaling Calculations. Phys. Rev. B 2001, 64, 235111.

[5] C. Jin, H. Lan, L. Peng, K. Suenaga, S. Lijima, Deriving carbon atomic chains from graphene, Phys. Rev. Lett 102 (2009)

[6] L. Ravagnan, N. Manini, E. Cinquanta, G. Onida, D. Sangalli, C. Motta, M. Devetta, A. Bordoni, P. Piseri, P. Milani, Effect of axial torsion on sp carbon atomic wires, Phys. Rev. Lett. 102 (2009)

[7] P. Avouris, Z. Chen, V. Perebeinos, Carbon-based electronics, Nature Nanotechnology 2, 605 - 615 (2007)

[8] E. B. Jochnowitz, J. P. Maier, Electronic Spectroscopy of Carbon Chains, Annu. Rev. Phys. Chem. 59:519-44 (2008)

[9] P. Thaddeus, M. C. McCarthya, Carbon chains and rings in the laboratory and in space, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, Volume 57, Issue 4, Pages 757-774 (2001)

[10] M. Jones Jr. , Organic Chemistry W. W. Norton, New York (2005)

[11] Q. Fan, G.V. Pfeiffer, Theoretical Study of Linear C_n (n=6-10) and HC_nH (n=2-10) Molecules, C Chem. Phys. Lett. 162, 472 (1989)