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Clar−Kekulé Structuring in Armchair Carbon Nanotubes

Francisco J. Martín-Martínez, Santiago Melchor, and José A. Dobado*

Grupo de Modelización y Diseño Molecular, Departamento de Química Orgánica,
Facultad de Ciencias, Universidad de Granada, 18071, Granada, Spain

dobado@ugr.es

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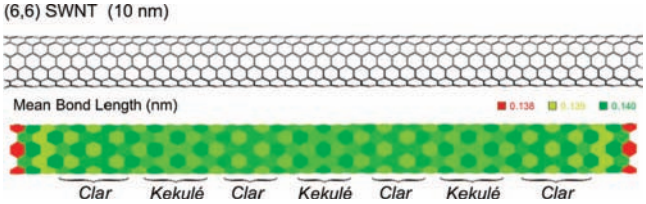
ABSTRACT



Geometrical patterns on armchair nanotubes and their dependence on length (up to 10 nm) have been studied using first-principles methods. The results indicate that finite nanotubes do not show a uniform bond structure. The previous structural classification of armchair nanotubes in Clar, Kekulé, and incomplete-Clar types becomes unified with lengthening, not in a bond-uniform structure, as PBC models report, but into an alternated sequence of Clar and Kekulé domains in all cases, with possible mechanical and electronic consequences.

Carbon nanotubes[1–4] (CNTs), which present remarkable conductive and mechanical properties,[5–7] are extremely long, with a diameter/length ratio of about 1:1.000. However, these are not infinite, but finite, and therefore, they always present a border. Due to their proportions, these are generally considered to be monodimensional crystals and are usually modeled accordingly by periodic boundary condition (PBC) calculations. These models have provided an enormous amount of information, offering an understanding of their main properties. Nevertheless, recent ab initio and DFT studies applied to CNT fragments have pointed out some dissimilarities between infinite and finite models.[8–12] In this paper, we describe the geometrical arrangement found in armchair nanotubes arising from their finiteness, and explore the extent to which the presence of CNT endings may affect the bonds of the overall molecular system.

If CNTs are considered infinite, their bonds can be only distinguished by their relative orientation with respect to the nanotube's longitudinal axis. This differentiation arises from a symmetry break in the graphite sheet after rolling it into a cylinder, which, for the higher symmetry armchair and zigzag CNTs, turns out to discriminate only two different bonds.[13] Tight-binding calculations reveal how the two different C−C bond lengths are arranged in the armchair and zigzag infinite CNTs: zigzag CNTs are characterized by *trans*-polyethylene chains encircling the nanotube, connected through shorter C−C bonds,[13,14] while in armchair CNTs the *trans*-polyethylene chains run along their tubular structure, bonded through longer bonds.[15]

In any case, the bond equivalence of infinite CNTs, strictly speaking, does not apply to finite fragments. However, it is

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reasonable to assume that, once the CNT is long enough, finite and infinite models shall converge, although it is not known at which length this would happen.

As mentioned above, there are calculations on finite CNTs which report geometric[8–12,17] and electronic[18,19] features that are caused by the close presence of the border. Some of these differences diminish progressively as the CNT fragment increases its length,[19] but other features, such as the geometric ones, have not yet been shown to attenuate in the same way. Intensive theoretical studies were made by Yumura et al.,[9–12] pointing out geometric patterns characterized by different bond lengths along the CNT. These patterns are much more remarkable for armchair CNTs than for any other chirality, presumably because of the particular geometric characteristics of its border, and these appear to transmute after any slight length variation.[8–12] Nakamura et al.[8] also observed these length-dependent geometric periodicities, which led them to classify the armchair CNT fragments according to length as Clar, Kekulé, and incomplete-Clar[20] types. Other geometrical arrangements were proposed by King[21] using Clar aromatic sextets.

According to Nakamura,[8] considering each bond in the structure with no extrapolation from infinite-length CNTs is necessary. Therefore, we should wonder about whether the bonds in CNTs retain the geometric, mechanical, and electronic properties predicted for infinite models, and thus, we are using first-principles theoretical methods to study CNTs. However, an analysis of the geometrical results without the adequate interpreting tools is a difficult task. For a thorough investigation of bond distortions, we have developed a geometrical analysis tool for graphite structures.[22] This involves two ring-averaged parameters, the ring bond dispersion (RBD) and the mean bond length (MBL) (see the Supporting Information for its definition) and are color coded in Figures 1–3. Figure 1 illustrates the two prototypical Clar and Kekulé bond arrangements,[23] together with the color convention employed in this work. Although both present uniform rings (red in RBD plot), the Clar rings have a reduced average bond length and consequently they are surrounded by bigger rings (yellow rings surrounded by green ones in MBL plot). On the other hand, in Kekulé bond alternation, uniform rings are bigger because neighbor rings have three bonds with higther double-bond character (green rings surrounded by yellow ones). This difference is the main clue for guessing where the Clar and Kekulé domains are located in CNTs.

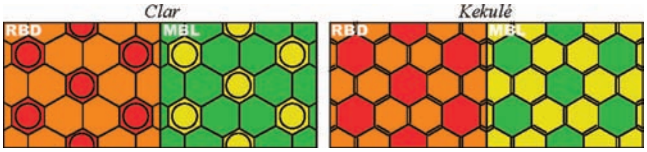

Figure 1. Illustration of prototypical Clar and Kekulé bond arrangements, where ring uniformity (top) and ring mean size (botton) are color coded.[16]

To ascertain how and to what extent edge effects determine the CNT geometry, we have performed DFT calculations with NWChem 5.0 program[24,25] on (6,6) armchair CNT fragments up to 10 nm long. B3LYP[26,27] methodology was employed together with the STO-3G*, 3-21G*, and 6-31G* basis sets.[28] For clarity, we notate the length of (*i*,*i*) armchair nanotubes with the number *u* of slices composing the tube, each of them containing 2*i* atoms. So, CNTs notated this way present the molecular formula $C_{2iu}H_{4i}$.

First, we considered a set of three (6,6) CNTs of about 5 nm long, each tube belonging to Clar, Kekulé, and incomplete-Clar types (**1**, $C_{468}H_{24}$; **2**, $C_{480}H_{24}$; **3**, $C_{492}H_{24}$) which are formed by 39, 40, and 41 units, respectively. In a second stage, an equivalent set of three CNTs of about 10 nm long was studied (**4**, $C_{972}H_{24}$; **5**, $C_{984}H_{24}$; **6**, $C_{996}H_{24}$) composed of 81, 82, and 83 units, respectively.[29]

Finally, the local stability of **3** has been checked, and no imaginary frequencies were presented (see the Supporting Information).

Figure 2 displays the optimized geometries and bond histograms of **1**, **2**, and **3** CNTs which were, in principle, representative of Clar, Kekulé, and incomplete-Clar types. The RBD plot reveals that **2**, being a Kekulé CNT, is noticeably different from the other two (**1** and **3**). Red rings (uniform) appear for all CNT fragments, but only in CNT **2** are these distributed evenly along the whole structure, without any sign of decay toward tube uniformity around the central region. However, **1** and **3** show the red dots in

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(16) Colors match the other figures in this letter, in order to facilitate the detection of Clar and Kekulé domains in CNT fragments.

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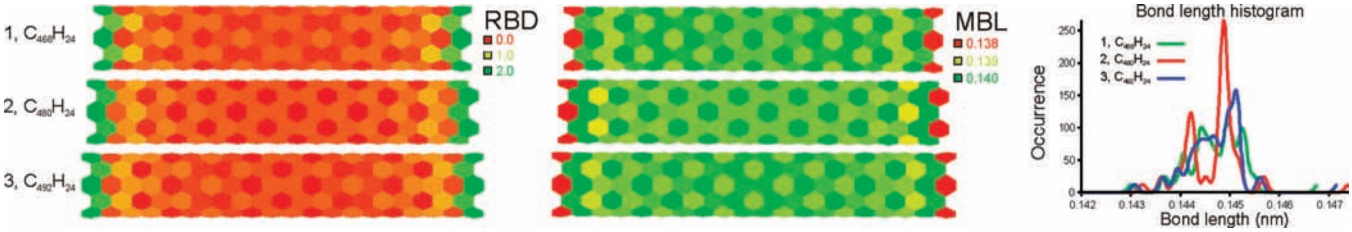

Figure 2. RBD (in 10^{-3} nm), MBL (in nm) and bond histogram representations, for (6,6) CNTs 1−3, calculated at the B3LYP/STO-3G* level.

more scattered positions and do not show the expected patterns described by Nakamura. A more detailed inspection of the RBD plot reveals that, for CNT **1**, uniform rings appear every four hexagons along the tube axis, while in **3** it seems that most red rings appear grouped only in the middle and near the ends of the CNT fragment. Nevertheless, in both cases, **1** and **3** seem to present an oscillation in the bonding pattern, with a continuous variation from Clar to Kekulé bonding schemes and vice versa. These arrangements, described for **1** and **3**, constitute neither an incomplete-Clar nor a Clar pattern, which could indicate the appearance of an additional trend dependent on nanotube length.

In the MBL plot (Figure 2), for Kekulé structure **2**, the uniform rings have greater size (dark green), which indicates the more single character of these bonds. At the same time, these rings are interconnected through shorter bonds with a higher double contribution, constituting a typical Kekulé arrangement. On the other hand, in the MBL plot, central part of **1** and **3** are somewhat complementary. In **1**, the uniform rings are encircled by smaller rings (depicted in light green), as opposed to the situation in **3**. Therefore, this central part of structure **1** is of the Kekulé type and in **3** is of the Clar type.

Bond histograms[30] reveal that the bonds are distributed in the 0.143−0.146 nm interval, but for **2**, there are two distinct bond lengths with high occurrence, at 0.144 and 0.146 nm. On the contrary, for **1** and **3**, the broad distribution caused by the gradation between Kekulé and Clar areas implies a great number of bonds with intermediate lengths, thus filling the center of the histogram.

The oscillating behavior presented in **1** and **3** could be expected for **3**, which would fit the incomplete-Clar description, but not for **1**, presumed to be a Clar one. Incomplete-Clar structures, as described by Nakamura, present a deficient distribution of Clar sextets, so this particular arrangement could be an expression of its incompleteness. However, Clar CNT **1** presents a severe degradation in comparison with a typical Clar area.

We have seen here that some of nanotube types defined by Nakamura have dissapeared at 5 nm. The unexpected behavior of the tubes' inner part lead us to wonder if this trend is maintained at higher tube lengths. Considering the computational resources available, we made calculations on 81, 82, and 83 unit CNTs (**4-6**) (Figure 3).

The most relevant fact in Figure 3 is that **5**, which was supposed to be a Kekulé type, like **2**, is not so any more, as happened before with structure **1**. Moreover, as in **1** and **3**, the Clar and Kekulé sections appeared for all **4**−**6** structures. Therefore, the Kekulé arrangement, although persisted at 5 nm, has not survived at 10 nm, and now all of them share the Clar−Kekulé oscillations. Consequently, neither Kekulé nor Clar arrangements by themselves seem able to cover extended areas in graphite structures, and domains of each pattern are alternated consecutively along the tubular structure in an oscillating fashion, with quite undefined frontiers between each type of domain.

The frontiers between Clar and Kekulé domains recall the Phason line concept, developed by Osawa et al. for fullerenes.[31] They reported a trend for the stability of fullerenes which is related with the length of these phason lines and the number of nodes.[32] According to that, structures with fewer nodes and longer phason lines are more stable and therefore the most frequent. Our results indicate that the number of Clar−Kekulé frontiers generally rises as the nanotube length grows, and hence, if these frontiers could be considered as phason lines, the existence of Clar−Kekulé oscillations would be the result of a particular CNT stabilization. In other words, a tubular structure would be most stable when the number of Clar−Kekulé frontiers is at a maximum because the added length of all the nodeless phason lines is also at a maximum.

Consequently, the number of Clar−Kekulé frontiers or phason lines can be used to characterize the tubular structures. This, applied to the studied CNTs **1**−**6**, results in the appearance of 4, 0, 2, 4, 6, and 8 frontier lines, respectively, which illustrates how difficult is to relate the number of domains with the CNT length. However, 10 nm structures share in common the alternation of consecutive Kekulé and Clar domains along the tube.

Given the necessity of a proper definition of Clar and Kekulé areas, we are currently developing a parameter to rationalize these oscillations. Such a parameter could allow

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(30) Histograms represent the occurrence of different bond lengths acting as a fingerprint for each specific CNT.

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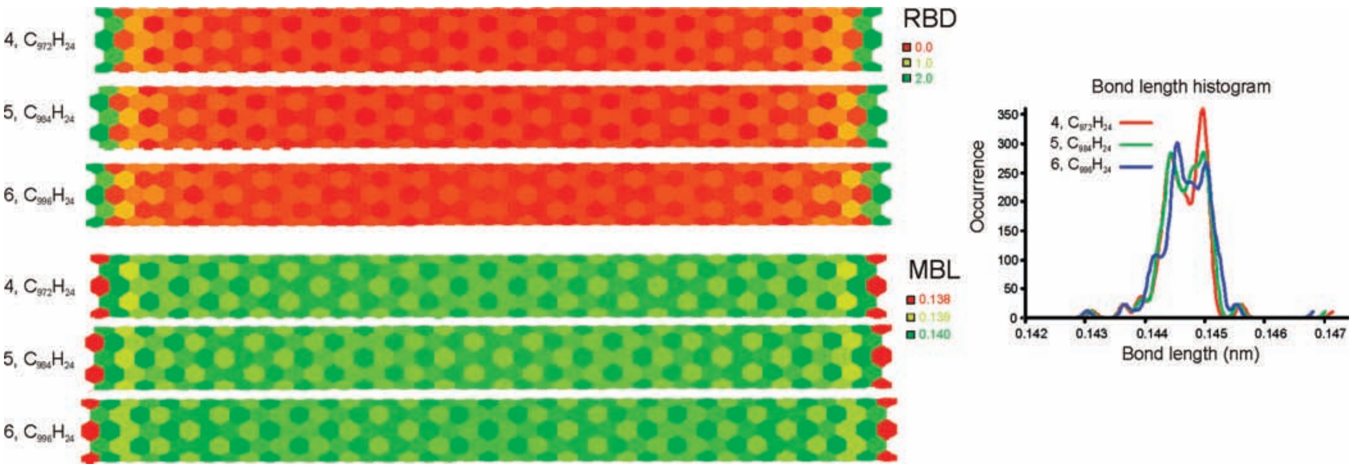

Figure 3. RBD, MBL, and bond histograms for structures **4**−**6**, (6,6) CNTs calculated at the B3LYP/STO-3G* level.

the generation of accurate CNT geometries,[33] and will be available soon.

In summary, armchair CNT fragments are not geometrically uniform as might have been expected, partially because of their finite-structure nature, but also because of their intrinsic bond arrangement. For CNTs up to 10 nm in length, DFT calculations indicate the presence of alternating Clar and Kekulé domains (Clar−Kekulé oscillations) even far from the border. These results are independent of the chosen basis set and were found without symmetry restrictions that could mask eventual geometrical effects.

Furthermore, although smaller CNTs fulfill the Nakamura classification, this appears to be adequate only for relatively short CNT fragments. However, once the CNT is long enough, Clar−Kekulé oscillations appear recurrently in all cases, suggesting the persistance of this structuring for even longer CNTs. Although it is quite clear that the border causes geometrical disturbances, edge effects seem to be limited beyond a certain distance from the border. Thus, once this limit is surpassed, the nanotube geometry does not prove uniform, as indicated by the results from widely used PBC infinite models, but it appears in the described Clar−Kekulé bonding scheme. Moreover, these limited edge effects suggest that the cause of these moved-away-from-the-border oscillations cannot be found in the existence of the border, but in an inherent bond arrangement of these graphite structures.

If this is the case, several fundamental questions arise. Could these oscillations be present on infinite or macroscopic-size nanotubes? Given that this phenomenon has not been yet confirmed experimentally, further theoretical studies are required to back up or discard this hypothesis. For that purpose, finite-sized models with detailed consideration of the whole structure, or infinite models with extended unit cells (comprising at least two joined Clar and Kekulé types) are necessary.

If Clar−Kekulé structuring receives further proof, this could have relevant consequences in the knowledge of CNTs. If bonds differ within a nanotube, both mechanical and electronic behavior are expected to change, as any external force applied on the CNT structure would result in a different response of the Kekulé and Clar domains. Also, the presence of Clar aromatic sextets on a fraction of the CNT would invariably affect both its electronic and chemical behavior.

Further analyses on this topic are currently underway, but from what is already available, the surprising structuring found here challenges the infinite models commonly employed on CNTs, which could nevertheless be enhanced by considering the effects discussed here. Given the relevance of CNTs in current research worldwide, the origin of Clar−Kekulé structuring deserves a conclusive explanation for a better understanding of the nature of CNTs.

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Supporting Information Available: Optimization details. Validity of the basis set used. TubeAnalyzer program details. Frequencies for compound **3**. PDB files of compounds **4**−**6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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