

Hydrocarbon chains and rings: bond length alternation in finite molecules

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Abstract We present a theoretical study of Peierls distortion in carbon rings. We demonstrate using the Longuet-Higgins–Salem model that the appearance of bond alternation in conjugated carbon polymers is independent of the boundary conditions and does in fact appear in carbon rings just as in carbon chains. We use the Hartree–Fock approximation and density functional theory to show that this behaviour is retained at the *first principles* level.

Keywords Peierls distortion · Conjugated polymers · Annulenes · Longuet-Higgins–Salem model · Density functional theory

1 Introduction

Peierls distortion [1] in one dimension (1D) is an inherent trait of linear conjugated polymers, leading to a bond length alternation (BLA). The usual chemical nomenclature for it is conjugation. Examples include polyacetylene and polyynes, two materials which have been studied by the physics and chemistry community for a very long time (see, e.g. the book [2] and the papers cited therein). For

more recent publications about the BLA in carbon chains, see, e.g. Refs. [3–6] and references therein. Polyynes in particular remains a hot topic experimentally and theoretically, in part due to the difficulty in determining the band gap of this material [6]. One reason why it is difficult to correctly calculate the band gap in Peierls distorted systems is that the bond length alternation directly determines the band gap, i.e. if the bond length alternation is underestimated (as is often the case in, e.g. density functional theory), the band gap will be underestimated as well. As such, the matter of correctly describing bond length alternation is a current and important topic.

In addition, Peierls distortion brings with it some interesting fundamental questions, such as whether the bond length alternation appears in carbon *rings*. It is known that in long linear chains, as we increase the length of the chain, we approach the infinite polymer where the Peierls distortion is realized. However, the effect cannot depend on the boundary conditions, and hence, a hydrogen terminated finite chain and a cyclic carbon ring must converge to the same Peierls distorted geometry in the infinite limit. All that can be different is the speed of convergence. In this work, we discuss the question of Peierls distortion in carbon rings and at what number of carbon atoms the alternation appears.

The BLA in conjugated polymers can be very well described by an improved Hückel-type method, the semiempirical Longuet-Higgins–Salem (LHS) model [7, 8].¹ The corresponding solid-state physics approximation is the Su–Schrieffer–Heeger model [9, 10]. The relationship between the LHS and the SSH models was pointed out in Ref. [11].

¹ Developing the model and the corresponding HUGE code and applying it to various conjugated polymers was a very fruitful collaboration between P.R. Surján and J. Kürti.

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To further demonstrate the robustness of the appearance of the Peierls distortion, we also use *ab initio* (Hartree–Fock, HF) and *first principles* (density functional theory, DFT) methods.

We start our investigation with the benzene molecule, where no BLA appears. We increase the number of carbon atoms by four atoms in each step in order to topologically allow the potential appearance of a BLA. Our goal is to find the critical number of carbon atoms where the ring becomes Peierls distorted. As it will turn out, it is not enough to consider only the simplest planar rings. Therefore, we consider various possible ring-type structures, determining their optimized geometries. The next section discusses which molecules come into question. This is followed by the results for the energies and for the BLA, starting with the LHS model, continuing with HF and DFT results. The paper is concluded by a summary.

2 Investigated molecules

Theoretically, the simplest possible carbon systems showing BLA are linear carbon chains with sp^1 hybridization. Imagine a row of carbon atoms where each atom is covalently bonded to its left and right neighbours. The question is, are the bond lengths uniform, or do they vary? Theoretically the purest case is the infinite long carbon chain. It can be shown, based on solid-state physics arguments, that for the infinite long chain the structure with alternating bond lengths (polyyne) is energetically more favourable than the structure with uniform bond lengths (polycumulene)—this is an example of the well-known Peierls distortion [1, 12]. However, this is only a speculative situation. In fact the longest isolated linear carbon chain consists of ‘only’ 44 carbon atoms [13], which is still far from a length which can be considered as infinite. The structure of a finite chain is strongly influenced by how it is terminated. The chain can be stabilized by relatively large end groups [13] or it can simply have a nitrogen atom or a hydrogen atom at the end [14]. There is even the possibility that the chain has no end groups, consisting of only carbon atoms [15, 16]. However, the accurate treatment of pure carbon molecules is a delicate problem which is outside the scope of this paper. We just mention that a linear C_n molecule is unstable against bending, crosslinking, forming fused rings or cage-like molecules, depending on the number of carbon atoms. The relatively long carbon chains are stable and accessible for experiments only if they exist inside carbon nanotubes [3, 17] or if they are separated from each other by alkali fluoride particles when preparing them from polytetrafluoroethylene [18, 19]. In any case the end groups have a drastic influence on the bond length alternation. For example, $H-C\equiv$ group or $N\equiv C-$ group at the end immediately triggers the BLA starting from the end of the chain. Therefore, the BLA is always present in linear

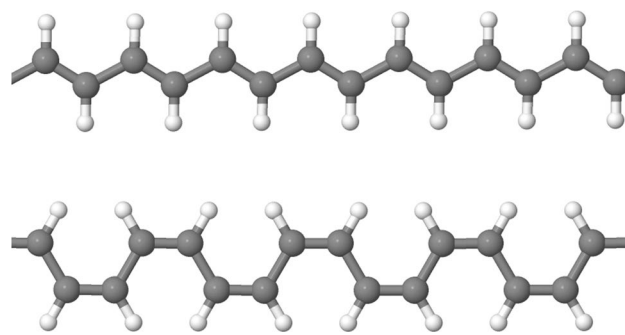


Fig. 1 *Trans* (*trans-transoid*) and *cis* (*cis-transoid*) isomers of polyacetylene, *above* and *below*, respectively

carbon chains, and only its amount changes (decreases) when going from finite molecules to the infinite limit. We can say, with some exaggeration, that qualitatively nothing special happens in this case.

The situation is more intriguing if we go from sp^1 to sp^2 molecules, that is, to hydrocarbons. Polyacetylene $(C_2H_2)_x$ is the prototype of the whole family of conjugated polymers. It has two isomers, the *trans* and *cis* forms (see Fig. 1). The *trans* isomer is more stable than the *cis* one. The experimentally observed bond lengths are 136/144 and 137/144 pm for *trans* and *cis* isomers, respectively. [Note that these bond lengths differ from that of ‘true’ double bond (133 pm) and single bond (154 pm)].

The BLA of the infinitely long polyacetylene can be reproduced theoretically on different computational levels: the LHS model gives a result of 136/144 pm for the bond lengths [8, 20], whereas the DFT method with B3LYP functional results in a BLA of 5 pm [12]. The BLA of short conjugated oligoenes is larger than this, again due to the chain end effects. The shortest oligoene 1,3-butadiene (C_4H_6) has bond lengths of 134 and 145 pm at the end and in the middle, respectively [12]. The next non-radical oligoene is 1,3,5-hexatriene (C_6H_8) with bond lengths of 134, 146 and 137 pm, starting from the edge.

End-group effects are completely avoided when we investigate closed (cyclic) conjugated molecules, that is, rings instead of chains. For an infinite long system, its properties should not depend on the boundary conditions. The question is what happens with the BLA for finite molecules. This is especially interesting in the case of sp^2 hydrocarbons. Benzene (C_6H_6) is a peculiar system. It is an aromatic molecule with D_{6h} symmetry, and hence, all six bonds are perfectly identical in length (140 pm). Our aim is to gradually increase the size of the ring in order to find the critical size where the bond alternation appears. However, this is not so straightforward as one would naïvely think it is.

First of all, we restrict ourselves to $C_{4n+2}H_{4n+2}$ monocyclic, unsaturated hydrocarbon molecules with $n = 1$ to

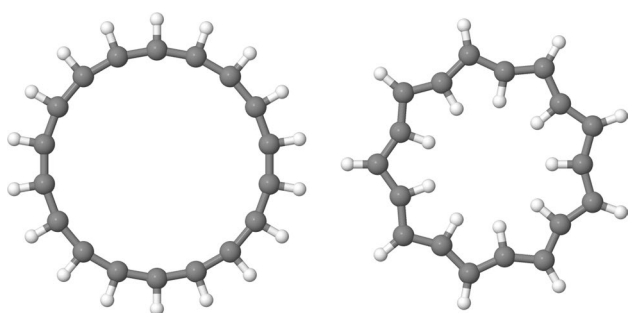


Fig. 2 [18]Annulene planar *all-cis* geometry (left) and [18]annulene planar *all-trans* geometry (right)

8 and 16. In other words, we consider annulenes, those ones which obey the Hückel's rule. Otherwise, the molecule cannot be aromatic, so there is ab ovo a bond length alternation. The next question is whether these molecules are planar or not. For the LHS model, this does not matter. In Hückel-type calculations, only the bond lengths play a role. However, for more sophisticated methods we need to know the precise spatial structure in three dimensions (3D). Therefore, we consider several possible configurations which correspond to local energy minima. Note that the structure of annulenes has been the subject of extensive research, see. for example, Refs. [21, 22].

The simplest case is the planar configuration, similar to the structure of benzene (see Fig. 2 left side). We call this *all-cis* structure. However, there are problems with the *all-cis* configuration. First, increasing the number of carbon atoms leads to an increasing deviation from the optimal 120° bond angle, that is, an increasing angular strain is induced. Second, the structure does not converge to that of the polyacetylene chain in the infinite case because all H atoms are on the same side of the carbon backbone. Even more, the *all-cis* structure is unstable in plane, as we will see later on.

Therefore, we consider the planar *all-trans* structures, as well (see Fig. 2 right side). Although this is very unfavourable for small rings (it is impossible, e.g. for benzene), it becomes, as opposed to the *all-cis* case, more and more favourable with increasing size, and, at the end, it converges to the structure of the *trans*-polyacetylene chain for the infinite case. Nevertheless, the *all-trans* structures are also unstable in a planar configuration, at least for not too large rings, as we will see later on.

We consider further structures as well. We optimize the geometry in 3D for [10]annulene (cyclodecapentaene = $C_{10}H_{10}$) and for [14]annulene (cyclotetradecaheptaene = $C_{14}H_{14}$). Figures 3 and 4 right side show that these molecules are indeed a non-planar structure in their relaxed geometries. It should be mentioned that these annulenes also have local energy minimum configuration where their

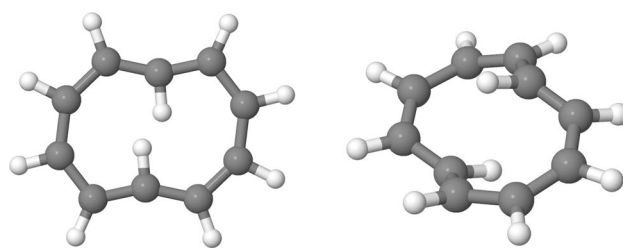


Fig. 3 [10]Annulene planar, optimized in two dimensions (2D) (left) and [10]annulene non-planar, optimized in 3D (right)

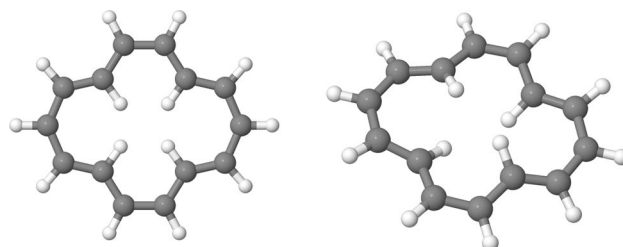


Fig. 4 [14]Annulene planar, optimized in 2D (left) and [14]annulene non-planar, optimized in 3D (right)

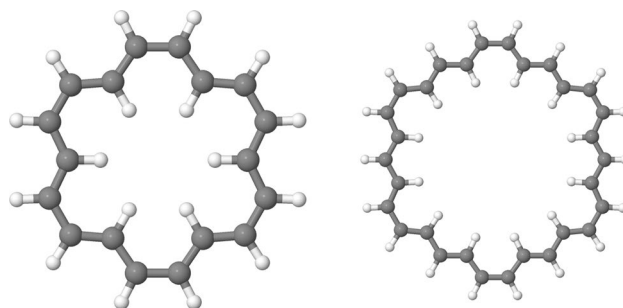


Fig. 5 Two annulenes with D_{6h} symmetry: [18]annulene- D_{6h} (left) and [30]annulene- D_{6h} (right)

structure is planar (see Figs. 3, 4 left side), but they are less favourable in energy than the non-planar ones in Figs. 3 and 4 right side.

The next annulene, [18]annulene (cyclooctadecanonaene = $C_{18}H_{18}$), is a special case. The most stable structure of this molecule is a planar aromatic structure with D_{6h} symmetry (see Fig. 5 left side). According to our geometry optimization, there are two slightly different carbon-carbon bond lengths: 140.0 pm (between carbons in *trans* position) and 141.6 pm (between carbons in *cis* position). In fact, according to Fig. 5 left side, one can define a whole family of rings. Introducing longer and longer *trans* segments between the six *cis* carbon pairs, the D_{6h} symmetry is retained. The $[6 + k \cdot 12]$ annulenes belong to this family. Figure 5 right side shows, e.g. the [30]annulene molecule

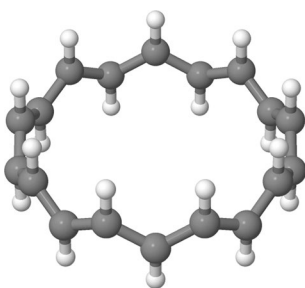


Fig. 6 [18]Annulene in nanoring form

with D_{6h} symmetry. Actually, with some indulgence, benzene can be regarded as the smallest molecule of this family, with no *trans* segments.

However, also the planar D_{6h} configurations are not without problems, because the bonds are symmetry inequivalent. The *cis* parts act as boundaries for the *trans* segments, so these molecules can be viewed as ones with internal delimiting effects, which can trigger the BLA even inside the *trans* segments. This leads us to consider *non-planar* hydrocarbon rings, with no end-group effects or internal delimitation (see Fig. 6 as an example). These $C_{4n+2}H_{4n+2}$ nanorings can be regarded as cut out appropriately from a $(4n+2, 0)$ zig-zag nanotube and hydrogenized. In other words, they can be viewed as a finite piece of *trans*-polyacetylene wrapped up *perpendicular* to

the plane of the polymer. They are energetically unfavourable for short rings. However, they become more and more stable with increasing size as we will see, and they develop into *trans*-polyacetylene in the infinite limit. Their advantage is that they are the adequate molecules to investigate the length dependence of the Peierls transition. Before Peierls distortion switches on, the molecule has $D_{\tilde{n}d}$ symmetry (where $\tilde{n} = 2n + 1$) and all bonds are symmetry equivalent. The ground state is degenerated, and the BLA can appear only by symmetry breaking.

3 LHS results

The LHS model originates from an early work of Longuet-Higgins and Salem [7]. The model was further developed by Surján [11] and Kertész [23] and by Surján and Kürti [8, 20, 24, 25]. It is a Hückel-type method in essence but with two important extensions. First, the β parameter of the Hückel method is not constant but depends on the bond length:

$$\beta(r) = -A \cdot \exp(-r/B). \quad (1)$$

Here the parameters A and B were optimized for carbon-carbon bonding so that the model can reproduce the BLA and the gap of *trans*-polyacetylene (see, e.g. in Ref. [8]).

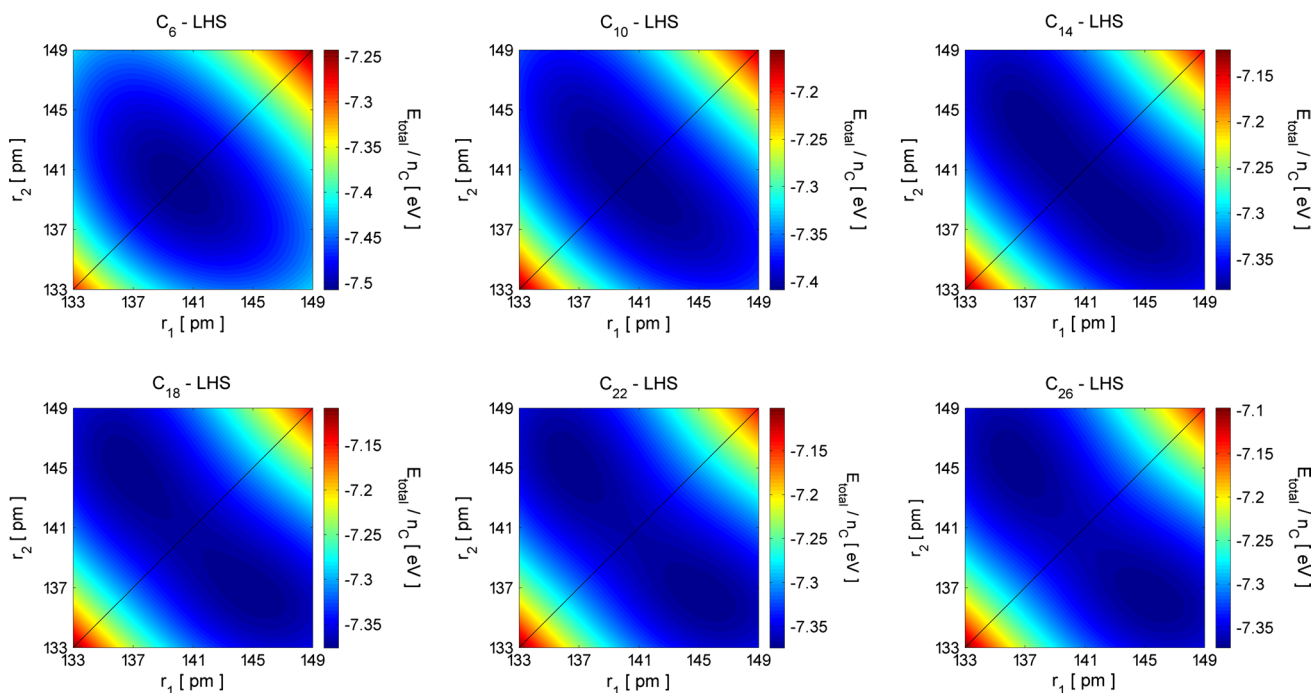


Fig. 7 Total energy per carbon atom contours for C_{4n+2} carbon rings as a function of the two consecutive bond lengths, according to the LHS model. The number of carbon atoms ($n_C = 4n + 2$) increases from 6 to 26 in steps of four atoms

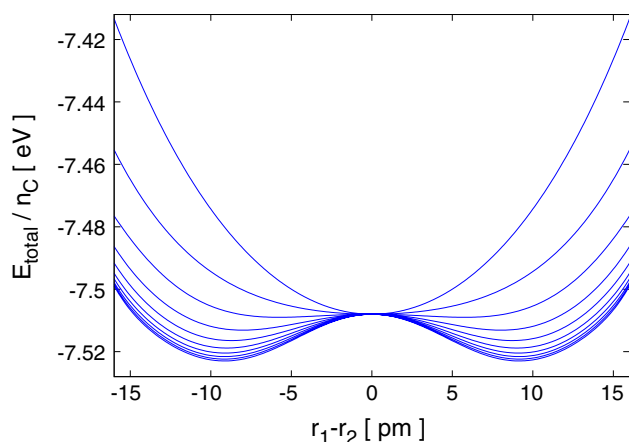


Fig. 8 Total energy per carbon atom for C_{4n+2} carbon rings versus bond length alternation, according to the LHS model. Increasing the number of carbon atoms ($n_C = 4n + 2$) from 6 to 42 in steps of four atoms results in a bifurcation. The BLA is initially zero and converges to $\approx \pm 9$ pm

The second important improvement is the explicit accounting for the σ -electrons by an empirical potential:

$$f_{\sigma}(r) = 2 \cdot \beta(r) \cdot (r - R_1 + B)/(R_1 - R_2), \quad (2)$$

where R_1 and R_2 are the lengths of the pure single and double bonds, respectively. This potential can be derived from, therefore is equivalent to, the empirical linear Coulson relation between bond length and (mobile) bond order [26]:

$$r = R_1 - (R_1 - R_2) \cdot p, \quad (3)$$

where p is the bond order for the π -electrons. The details of the model, together with some of its applications, can be found in the references mentioned above. We emphasize here only the most important property of the LHS method: as opposed to the usual Hückel theory, it allows the optimization of the bond lengths in a self-consistent manner by satisfying the Coulson relation, which at the same time minimizes the total ($\pi + \sigma$) energy. However, one has to keep in mind that the LHS model cannot handle the bond angles, only the bond lengths.

H atoms are neglected in this model. We used our LHS code to calculate the total energy of the C_{4n+2} rings, starting with $n_C = 4n + 2 = 6$ (benzene) until $n_C = 4n + 2 = 42$. We scanned the geometry according to dimerization, having only two independent bond lengths. The two consecutive bonds (r_1 and r_2) can be different, but all odd-numbered bonds are identical in length, as are all even-numbered bonds. Figure 7 shows the 2D total energy map, that is, the total energy per carbon atom contours as a function of the two neighbouring bond lengths, for rings C_6 to C_{26} . The maps are symmetric with respect to the $r_1 = r_2$ (BLA = 0) line.

The total energy has a stable minimum for C_6 and C_{10} at $r_1 = r_2 = 140$ pm. However, starting from C_{14} the minimum

with BLA = 0 becomes a saddle point and a Peierls distortion appears. This can be seen more clearly in Fig. 8. These 1D curves show the total energy per carbon atom along the line which is perpendicular to the BLA = 0 line and goes through the minimum point for $n_C = 4n + 2 = 6$ and 10, or through the saddle point for $n_C = 4n + 2 \geq 14$. For the sake of clarity, the curves are shifted so that they all have the same energy value in the BLA = 0 point. For $n_C = 6$ the total energy has a relatively sharp minimum, and for $n_C = 10$ the minimum is already very flat. Starting from $n_C = 14$ a bifurcation occurs which becomes more and more pronounced converging to BLA $\approx \pm 9$ pm.

4 HF results

We already mentioned that the LHS model cannot handle either the H atoms or the bond angles. It takes into account only the topology of the C atoms. To check the reliability of the LHS results, we repeated the calculations on a higher level using the Hartree–Fock approximation. In this case, one has to know the true geometry of the molecule. We carried out the HF calculations for the planar *all-cis* configuration of the $C_{4n+2}H_{4n+2}$ molecules with $n_C = 4n + 2 = 6, 10$ and 14. We used the G09 code [27] to calculate the total energy of these molecules. We repeated the same procedure what was done with the LHS model. We scanned the geometry according to dimerization, having only two free parameters, lengths of the two independent consecutive carbon–carbon bonds (r_1 and r_2). The lengths and angles for the C–H bond were kept fixed. Figure 9 shows the 2D total energy map, that is, the total energy contours as a function of the two neighbouring bond lengths, for $C_{4n+2}H_{4n+2}$ molecules with $n_C = 4n + 2 = 6, 10$ and 14. The energy values are defined as the total energy per carbon atom of the molecule minus the total energy per carbon atom for benzene. The maps are symmetric with respect to the $r_1 = r_2$ (BLA = 0) line.

The total energy has a stable minimum for C_6H_6 and $C_{10}H_{10}$ at $r_1 = r_2 = 139$ pm. However, for $C_{14}H_{14}$ the minimum with BLA = 0 becomes a saddle point and a Peierls distortion appears, with two different bond lengths of 137 and 146 pm (BLA = 9 pm), very similar to what was observed with LHS model.

5 DFT results

With the HF-method, we optimized only the positions of the carbon atoms. More reliable results can be obtained if one optimizes the structure by taking into account all geometrical degrees of freedom. This means not only the optimization of the positions of the H atoms but also allowing the molecule to distort out of plane. We

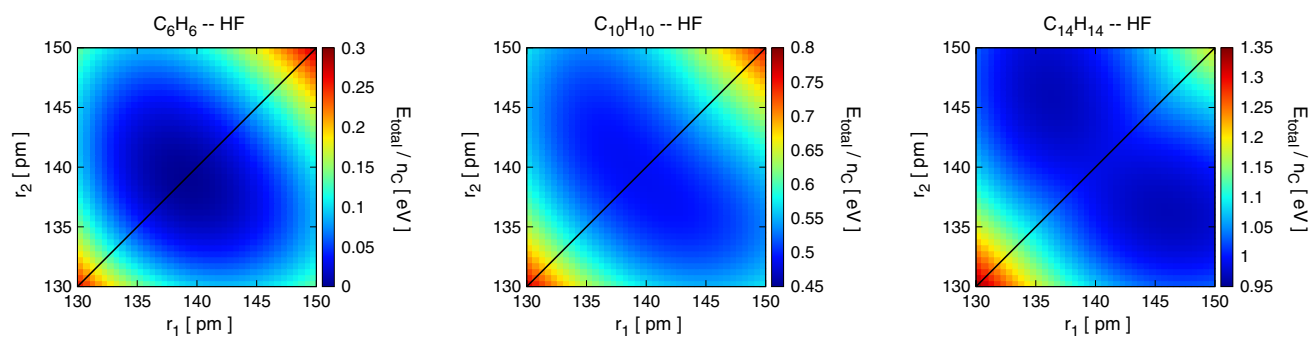


Fig. 9 Total energy per carbon atom contours for $C_{4n+2}H_{4n+2}$ planar *all-cis* rings as a function of the two consecutive bond lengths, according to the Hartree–Fock approximation. The number of carbon atoms ($n_C = 4n + 2$) increases from 6 to 14 in steps of four atoms

mentioned already earlier that in most cases the planar structure proved to be unstable. Our aim was to consider further ring configurations and to find possible structures in local energy minima. In order to do this, we have chosen density functional theory using the B3LYP/6-31G(d,p) functional of the G09 program package [27]. This *first principles* method already takes into account the correlation, but it is still manageable for molecules shown in Sect. 2.

We optimized the geometry with various constraints:

- The structure was relaxed in plane with *all-cis* geometry (see, e.g. Fig. 2 left part), for $n_C = 6, 10, \dots, 34$ and 66.
- The structure was relaxed in plane with *all-trans* geometry (see, e.g. Fig. 2 right part), for $n_C = 6, 10, \dots, 34$ and 66.
- The structure was relaxed in plane starting from the special sp^2 structure for $n_C = 10$ and 14 (see Figs. 3, 4 left parts).
- The structure was relaxed in 3D starting from the special sp^2 structure for $n_C = 10$ and 14 (see Figs. 3, 4 right parts).
- The structure was relaxed in plane starting from D_{6h} structure for $n_C = 18, 30$ and 66 (see Fig. 5 for $n_C = 18$ and 30).
- The structure was relaxed in 3D for nanorings with $n_C = 6, 10, \dots, 34$ and 66 (see, e.g. Fig. 6 for the case of $n_C = 18$).

As it was mentioned earlier, all molecules fulfil Hückel's rule: the number of C atoms is $n_C = 4n + 2$. Figure 10 shows the results for the calculated total energies per carbon atom. Benzene is the energetically most favourable structure, and its value was chosen as zero. Benzene belongs to two different families: it has an *all-cis* structure and D_{6h} symmetry at the same time. The energy of the *all-cis* series increases rapidly and starting from $n_C = 18$ they are the most unfavourable structures. Furthermore, they are unstable against

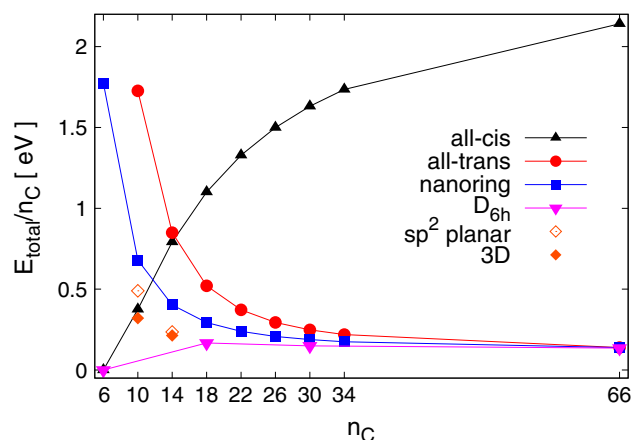


Fig. 10 Total energies per carbon atom obtained by B3LYP/6-31G(d,p) for various ring-type molecules shown in Figs. 2, 3, 4, 5 and 6. The obtained value for benzene was chosen as the reference point with zero energy. The lines are guides for the eye for the different families

out-of-plane distortions as it can be read out from the increasing number of imaginary frequencies in the vibrational analysis.

The behaviour of the *all-trans* series is reversed. It is very unfavourable in energy for small molecules, but its energy per carbon decreases with increasing n_C . Nevertheless, they are unstable against out-of-plane distortions. Interestingly, the *all-trans* structure will go over the nanoring structure for $n_C = 66$.

We investigated the special sp^2 structures, in planar as well as non-planar configuration, for $n_C = 10$ and 14. Their energies are quite favourable. Of course, the non-planar one is the most favourable structure, but the difference between the values for planar and non-planar case decreases when going from $n_C = 10$ to $n_C = 14$. For $n_C = 18$ they coincide and they are both identical with the D_{6h} structure. However, the bonds are symmetry inequivalent for these structures, even in the case of D_{6h} symmetry, with the only exception of

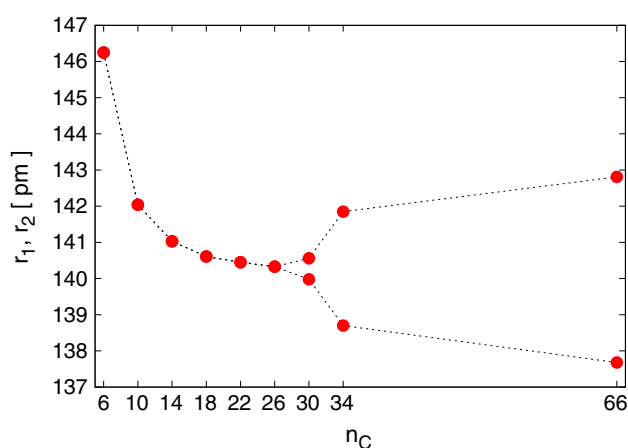


Fig. 11 Change of the bond lengths with increasing number of C atoms in the nanorings as obtained by B3LYP/6-31G(d,p). A bifurcation occurs at $n_C = 26$ and a finite BLA appears

benzene. Therefore, these molecules are not suitable for studying the appearance of Peierls distortion. (We mention that the D_{6h} symmetry lowers to D_{3h} symmetry for $n_C = 30$ and 66).

We arrive at the nanorings. As mentioned in Sect. 2, they are ring-like molecules with symmetry equivalent carbon-carbon bonds. The consecutive H atoms are all in *trans* position, and they lay not in the plane of the ring of C atoms, but perpendicular to this plane. The optimized geometry proves to be stable, without any imaginary frequency vibrational modes, until the largest nanoring we considered ($n_C = 66$). Due to the symmetry and the stability, the nanorings are the ideal systems to study the appearance of the bond length alternation. For small rings, until $n_C = 26$ there is no BLA in the molecule after geometry optimization. At $n_C = 30$ a bifurcation occurs and the BLA becomes finite. Figure 11 shows the evolution of the Peierls distortion in the finite system. The value of the BLA at $n_C = 66$ in the nanoring is 5 pm which is in very good agreement with the DFT calculated 5 pm BLA for infinite polyacetylene [12].

6 Summary

We investigated the appearance of bond length alternation (Peierls distortion in physical language, conjugation in chemical language) in closed sp^2 hydrocarbon molecules. For finite linear chains of the type $C_{2n}H_{2n+2}$ it is well known that short and long bonds alternate regularly (conjugated oligoenes). Although the BLA decreases with increasing chain length, it does not disappear but remains finite when the chain length goes to infinity. This means that there is no qualitative change in BLA when going from finite chains to the infinite chain. On the other hand, the situation is different

for closed annulenes. Here, a qualitative change occurs. Benzene has no BLA, and all bonds have the same length. However, for long enough rings there should be a bond length alternation, because in the infinite limit the properties should not depend on the boundary conditions, that is, it should not matter whether the system is open (chain) or closed (ring). We investigated theoretically the transition from non-alternating rings to alternating ones, as a function of the number of carbon atoms in the ring for $C_{2n}H_{2n+2}$ molecules. Calculations have been done on different levels of theory. With the Longuet-Higgins–Salem and the Hartree–Fock methods, this transition occurs rather soon: as few as 14 carbon atoms are enough and the BLA becomes nonzero. According to our DFT results with B3LYP/6-31G(d,p) functional, the transition shifts to larger rings: the appearance of the BLA occurs at $C_{30}H_{30}$. This result was obtained for ‘nanorings’ which are slices from zig-zag nanotubes, saturated by H atoms, where the H–C bonds are parallel with the symmetry axis of the ring. We investigated many cyclic structures, planar and non-planar both. The planar *all-cis* and *all-trans* rings are either energetically unfavourable or unstable, with the only exception of benzene. The annulenes with D_{6h} symmetry are energetically favourable, but here and in some possible 3D cases the bonds are not symmetry equivalent. Therefore, the investigation of Peierls distortion is without meaning. The only cyclic hydrocarbon molecules are the $C_{2\bar{n}}H_{2\bar{n}}$ nanorings with $D_{\bar{n}d}$ symmetry, which are energetically favourable and stable (except for the too small rings) and in which all carbon-carbon bonds are symmetry equivalent. The ground state is degenerate, and the BLA can appear only by symmetry breaking.

At the end, we mention that in the future there might be methods by which the planar structures, which are unstable in pristine state, can be stabilized by intercalation between the layers of 2D layered materials like boron nitride or transition metal dichalcogenide materials. Also the synthesis of hydrocarbon nanorings might be a challenge for preparative chemistry. Note that the synthesis of carbon picotubes [28] may be considered the first step in this direction.

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