

Stability and Properties of Polyhelicenes and Annulated Fused-Ring Carbon Helices: Models Toward Helical Graphites

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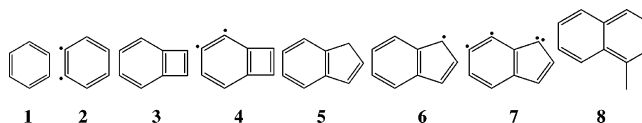
The geometrical structures and properties of conjugated polyhelicenes and annulated fused-ring carbon helices with analogous frameworks were theoretically studied at the HF/6-31G* and B3LYP/6-31G* levels. These studies focused on the stability of the fused-ring structures with special emphasis on the helical geometrical arrangements. To elucidate bonding patterns, the orbitals, electron density contours, and the electrostatic potential of these helical compounds were analyzed. The structure of fused polynaphthalenes arranged in a helical spiral can be regarded as part of a locally helical graphite lattice that is expected to give rise to special electronic properties along the helically layered conjugated single sheet that can be regarded as a single extended π system but also involving local layer-to-layer π – π interactions that are typical in ordinary graphite. This dual feature might lead to novel materials.

I. INTRODUCTION

Helicenes have attracted attention because of their special structural features and unusual chirality. More recently, such helically extended conjugated systems of fused rings have become a subject of interest in the context of design and synthesis of novel molecules and materials, potentially with a variety of unusual properties and applications. The helicenes, the first of which was hexahelicene reported by Newman and Lednicher in 1956,¹ are a special family of chiral molecules with exceptional optical activities and potential uses as nonlinear optical (NLO) materials as well as asymmetric catalysts.² Whitener's group synthesized the first helical phenylenes: angular [6]-, [7]-, [8]-, and [9]phenylene in 2002.^{3,4} The geometry and thermochemistry of phenylenes have also been investigated using ab initio methods,^{5–7} and several studies have focused on the relationship between proton chemical shift and aromatic or antiaromatic character,^{8,9} racemization barriers,¹⁰ chirality,¹¹ and optical properties.^{12–14} Some investigations on the synthesis of helicenes where some carbon atoms in the helical frameworks were replaced by other atoms such as sulfur were studied as well.^{15–17}

In the above studies, the [N]helicenes were limited approximately to a single turn of the helix, where the number of possible isomers had to be taken into account.⁸ In this work, the theoretical computational investigations were carried for up to double turn (anticlockwise) polyhelicenes and analogous, more extended structures formed by units of benzene, indene, and methylenynaphthalene. The annulated fused-ring carbon atom helices with frameworks analogous to ordinary helicenes were studied as well. In addition to

[N]helicenes, several types of analogous molecules were studied. Typically, [N]phenylenes and [N]polyindenes are comprised of helically extended conjugated π systems of alternating N benzene units fused to N-1 cyclobutadiene rings and alternating N benzene units fused to N-1 pentene rings. In this work, [6]- and [12]helicenes, angular [6]- and [12]phenylenes, helical [4]- and [8]polyindenes, helical [4]- and [8]dehydropolyindenes, annulated fused-ring all-carbon helices with frameworks analogous to the above helicenes, and helical [6]- and [12]polymethylenynaphthalene were optimized at the levels of HF/6-31G* and B3LYP/6-31G*. The geometrical structures (anticlockwise helical structures) are presented in Figures 1 and 2. The structural units corresponding to [N]helicenes, [N]dehydrohelicenes, angular [N]phenylenes, angular [N]dehydrophenylenes, helical [N]polyindenes, helical [N]dehydropolyindenes, helical [N]perdehydropolyindenes, and helical [N]polymethylenynaphthalene are given below



respectively. For brevity, in this paper, the helices built from N of these units **1** to **8** will be denoted by [N] helix (**1**) to [N] helix (**8**), respectively.

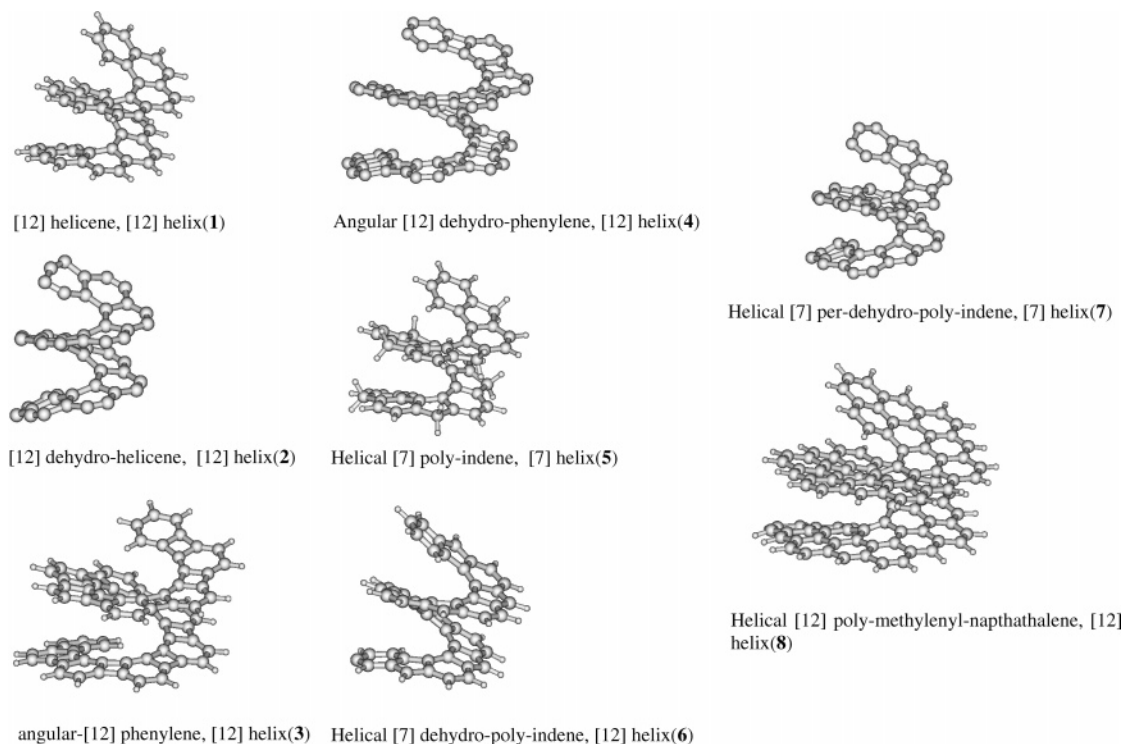
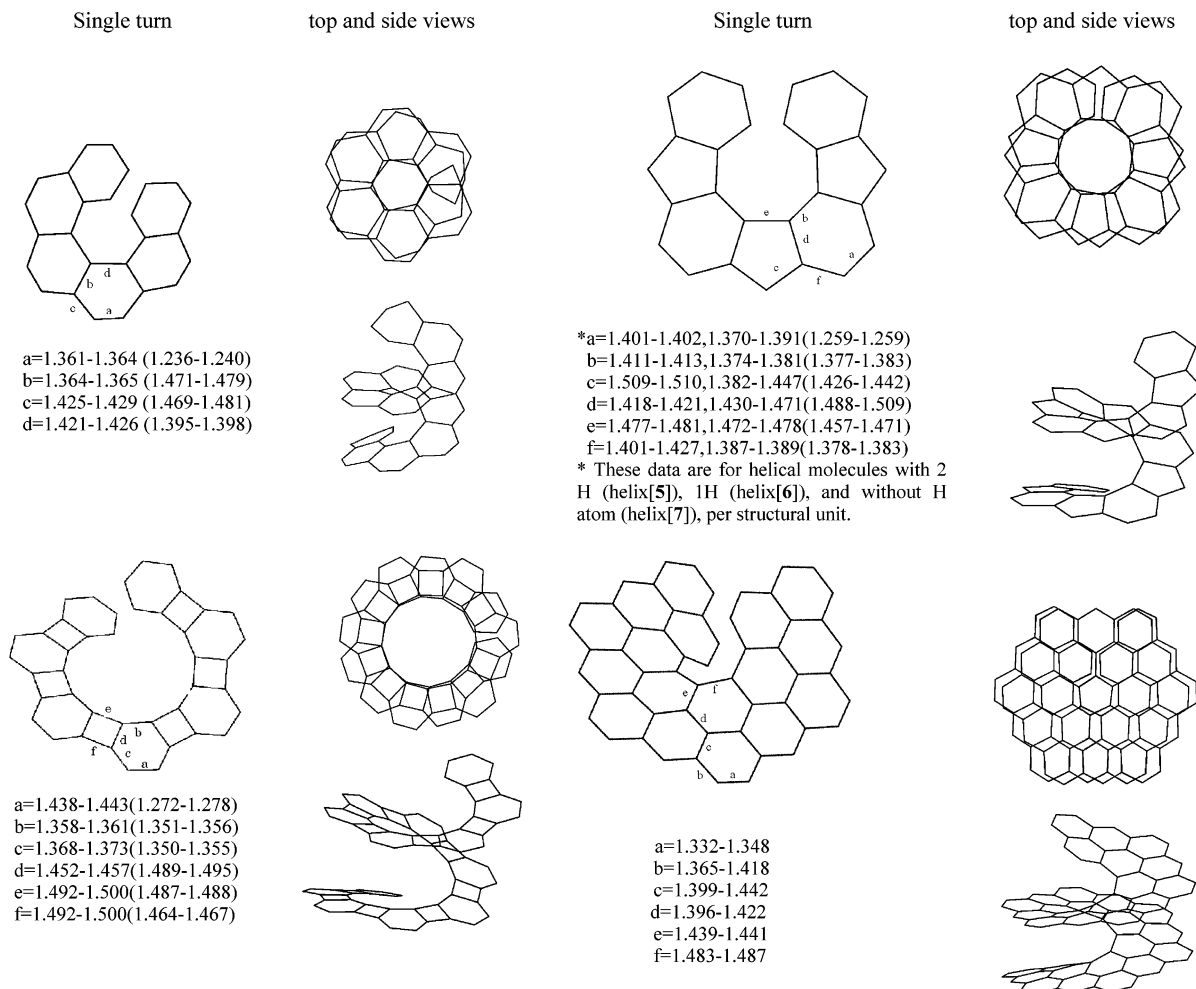
II. COMPUTATIONAL METHODOLOGY

The optimized geometries and stability were determined using GAUSSIAN 03¹⁸ with the 6-31G* basis set^{19,20} at the HF and B3LYP levels. For the characterization of energy minima, harmonic vibrational frequencies were calculated at the same level of theory. The electron density analyses were carried at the HF level with the 6-31G* basis set. The

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**Figure 1.** The geometries of [N] helices.**Figure 2.** Geometries and bond lengths of helicenes and fused-ring carbon helices with analogous frameworks.

single turns of helical molecules, with molecular isodensity contour surface of 0.05, 0.20, 0.29, 0.31, and 0.33 (a.u. =

e^-/bohr^3) are used to elucidate some of the essential features of the bonding patterns.

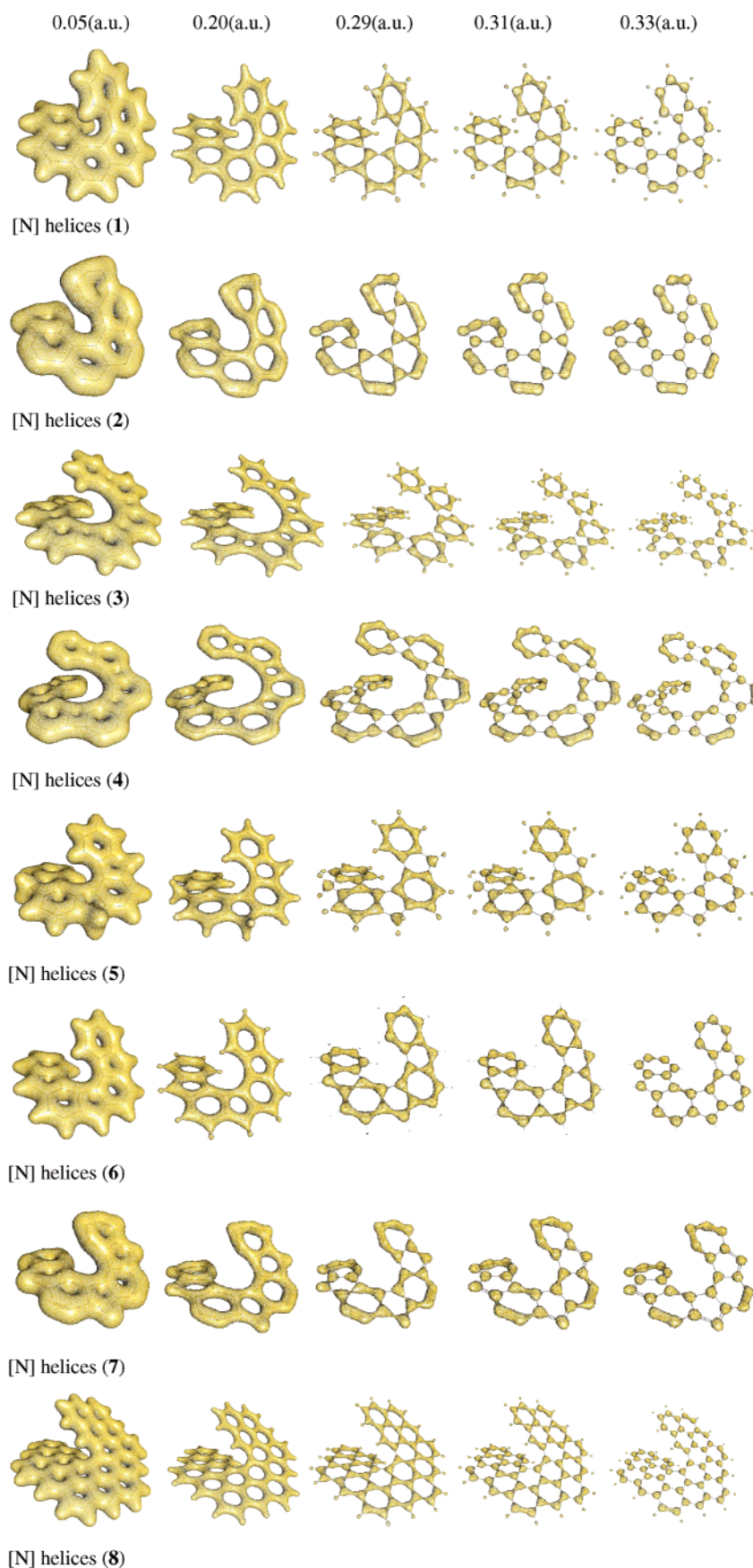


Figure 3. Electron density isocontours (a.u. = e^-/bohr^3) of polyhelicenes and annelated fused-ring carbon helices.

III. RESULT AND DISCUSSIONS

The computed optimum structures of the [6]- and [12]-helicenes and [6]- and [12]dehydrohelicenes are characterized

to be minima by having real frequencies for all eigenvectors of the Hessian at the B3LYP/6-31G* level. For nonterminal rings of the spiral, there are four kinds of carbon-carbon

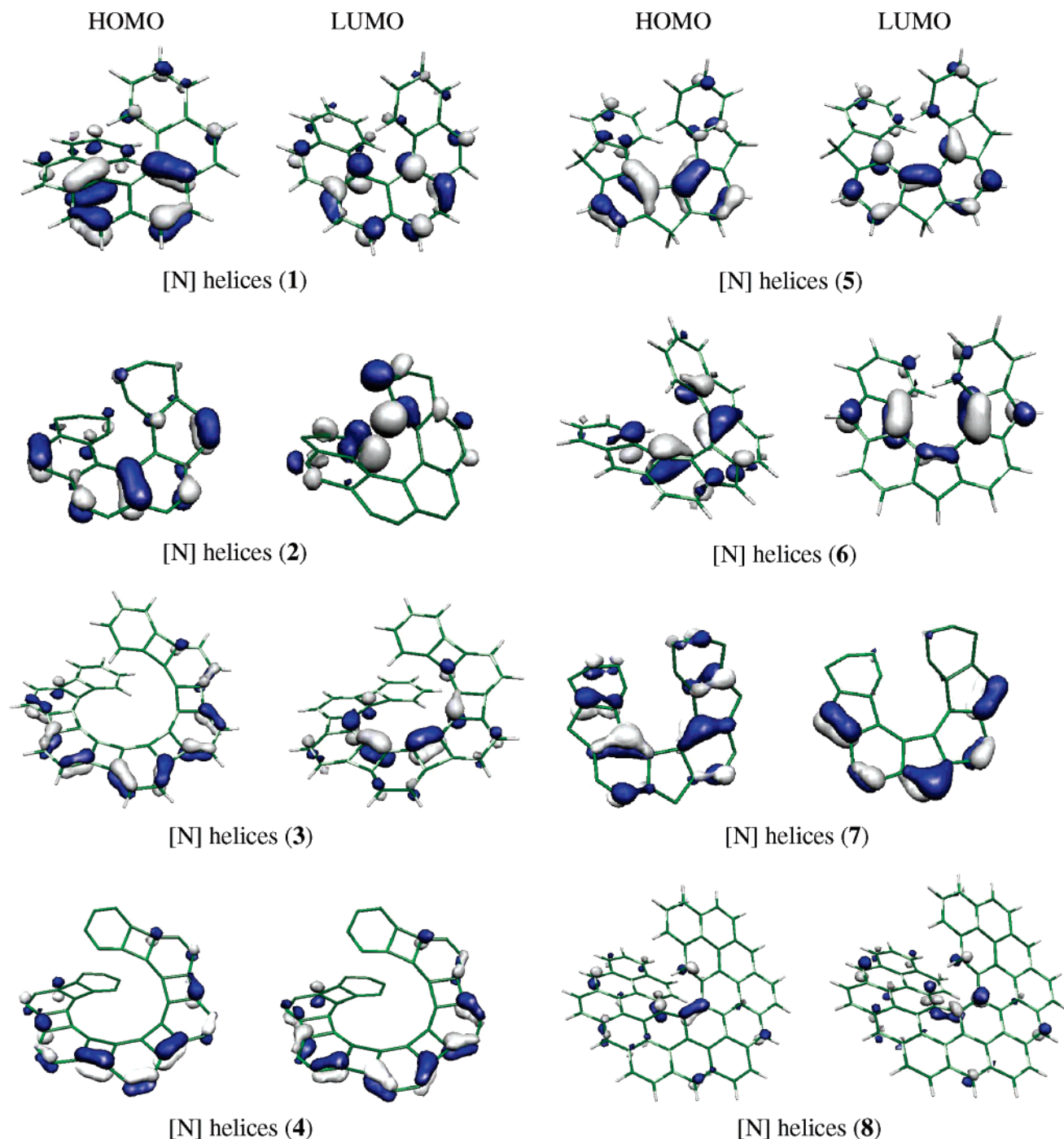


Figure 4. HOMO and LUMO of polyhelicenes and annelated fused-ring carbon helices.

bond lengths in the unit structure of [N] helix (1) and [N] helix (2) denoted by *a*, *b*, *c*, and *d* (see Figures 1 and 2). The bond lengths of helicene are close to those of carbon–carbon double bonds or fall between single and double bonds. The corresponding bonds of the carbon helices with analogous frameworks are significantly different from those of the related helicenes being similar in length to triple bonds or fall between single and double bonds. The two end-rings of fused-ring carbon helices show major deviations compared to the intermediate units of the helices. The results of detailed electron density shape analyses of molecules (Figure 3) are in agreement with those of bond length considerations. However, they provide better insight into the bonding pattern. When the isocontours of 0.29, 0.31, and 0.33 e^-/bohr^3 are considered, one finds that the order of bond strength for the

bond types are *d*, *c*, *b*, and *a*, respectively, in the [N] helices (1), where bond type *a* is the strongest. For the [N] helices (2), bonds *c* and *b* have almost the same electron density bonding pattern and *a* is again the strongest bond.

Angular [6] phenylene and angular [6] dehydrophenylene (both end units are benzene rings) were optimized to be minima confirmed by frequency calculations, while angular [12] phenylene and angular [12] dehydrophenylene correspond to stationary points that are apparently minima but are unconfirmed by frequency calculations at the level of B3LYP/6-31G* (Figure 1). There are six kinds of carbon–carbon bond lengths in the unit structure. The bond lengths in [N] helices (3) fall between single and double bonds, whereas the bond lengths in [N] helices (4) are either close to triple bonds or fall between single and double bonds. Each

turn of helices (3) and (4) contains more carbon atoms than the turns in helices (1) and (2), so helices (3) and (4) can be considered as less compact. The results of electron density analyses of the molecules agree well with the qualitative conclusions based on bond lengths. The isocontours of 0.29, 0.31, and 0.33 e^-/bohr^3 for the electron density correspond to a set of merging densities in the bond types of *e*, *f*, *d*, *a*, *c*, and *b* in [N] helices (3). The bond type *a* is the strongest in helices (4), showing already a continuous bond in the electron density isocontour of 0.33 e^-/bohr^3 in Figure 3.

Helical [4]- and [8] polyindenes (helices (5)) and helical [4] dehydropolyindenes (helices (6), both end units are benzene rings) were found to be minima and [8]dehydropolyindene to be a stationary point at the B3LYP/6-31G* level, respectively. The minima of helical [4] and [8] per-dehydropolyindenes, helices (7) were found as well at the same level of theory. There are six kinds of carbon-carbon bond lengths, *a*, *b*, *c*, *d*, *e*, and *f* in the unit structure. The bond lengths in [N] helices (5) are between those of single and double bonds. The electron density analysis of these molecules (Figure 3) is in agreement with the qualitative bond length considerations. The bonds of six-membered rings are stronger than those of five-membered rings in [N] helices (5), with bonds *c* and *e* being close to single bonds, and the electron density analysis shows a separation into hexagons with the increase of the electron density contour value from 0.29 to 0.31 e^-/bohr^3 . In [N] helices (5), the electron densities are quite different from those of [N] helices (6). Bonds of type *c* are shortened greatly on the hexagons in [N] helices (6) relative to [N] helices (5). When the isovalues are increased from 0.29 to 0.31 and to 0.33 e^-/bohr^3 , the bond types of *e*, *d*, *c*, *f*, *a*, and *b* in [N] helices (6) break step by step. Only bond *a* is significantly shorter in [N] helices (7) relative to [N] helices (5) and [N] helices (6).

For the last type of molecules, helices [6]- and [12] helices (8)—models toward helical graphites—the optimized geometrical structures are stationary points at the level of HF/6-31G* (Figure 1), and [6] helices (8) are characterized as corresponding to minima with all real frequencies at the HF/3-21G* level.

The goal of designing these structures is trying to gain some insight into a new type of materials tentatively termed “helical graphites”. The largest molecule designed in this study contains 34 fused hexagons. There are six kinds of carbon-carbon bond lengths in the unit structure (Figure 2), and they fall in length between single and double bonds. The results of electron density analyses of the molecules (Figure 3) show that the pattern of bond formation agrees well with simple qualitative, bond length considerations. There is an apparent possibility to construct much more extended helical sheets based on the result on [N] helices (8). A novel type of material of helical graphites with special electronic properties could be expected based on these results.

The analyses of orbitals with a focus on the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbitals (LUMO) are shown in Figure 4. Both are extended over large regions of the molecules which indicate that the large-scale electronic features of these molecules are likely to provide for unusual electronic behavior. The electrostatic potentials (ESP) of [N] helices (1), [N] helices (3), [N] helices (5), and [N] helices (7) are depicted in Figure 5 using electron density isocontour 0.02 e^-/bohr^3 and the

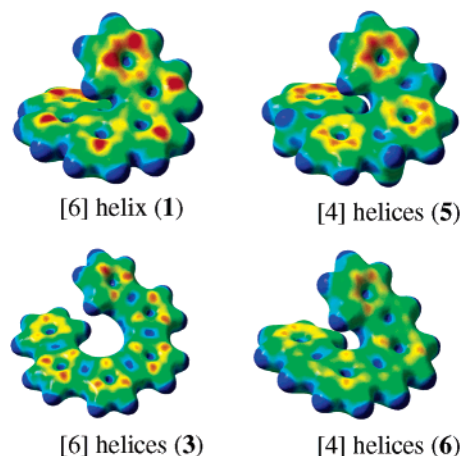


Figure 5. Electrostatic potential (ESP) of helical structures (isovalue = 0.02 e^-/bohr^3 , and the range of color bar is -0.01 – 0.1 ESP units).

range of color bar -0.01 – 0.1 for the electrostatic potential. The differences among the ESPs of these molecules indicate some degree of uniformity along the fused rings, but there are also marked differences along certain regions that could provide for different reactivities.

IV. SUMMARY

A family of helicenes and fused-ring carbon helices with analogous frameworks were investigated with a special focus on geometries, electrostatic potential, and electron densities of these extended conjugated systems. The predictions are encouraging, indicating that such molecules could provide useful novel materials with unusual electronic properties. The transfer of electrons along the helical conjugated sheets as well as across the layers through π – π interactions will be studied in our subsequent works. In a forthcoming study we shall address some of the bond order and energy aspects of the π – π interactions in these and similar structures.

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