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# Wavy carbon: A new series of carbon structures explored by quantum chemical calculations

Koichi Ohno[a,b,c,*], Hiroko Satoh[c,d,e], Takeaki Iwamoto[a], Hiroaki Tokoyama[f], Hideo Yamakado[g]

[a] Department of Chemistry, Graduate School of Science, Tohoku University, Aramaki, Aoba-ku, Sendai 980-8578, Japan
[b] Institute for Quantum Chemical Exploration, Minato-ku, Tokyo 108-0022, Japan
[c] National Institute of Informatics (NII), Chiyoda-ku, Tokyo 101-8430, Japan
[d] Research Organization of Systems and Information (ROIS), Minato-ku, Tokyo 105-0001, Japan
[e] Department of Chemistry, University of Zurich, 8057 Zurich, Switzerland
[f] Graduate School of Systems Engineering, Wakayama University, Sakaedani 930, Wakayama, Wakayama 640-8510, Japan
[g] Faculty of Systems Engineering, Wakayama University, Sakaedani 930, Wakayama, Wakayama 640-8510, Japan

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ABSTRACT

A new carbon family adopting wavy structures has been found by quantum chemical calculations. The key motif of this family is a condensed four-membered ring. Periodically wavy-carbon sheets (wavy-$C_n$ sheets, $n = 2$, 6, and 8) as well as wavy-$C_{36}$ tube were found to be very similar to the previously reported prism-$C_n$ carbon tubes ($n = 5$, 6, and 8) in several respects, including the relative energies per one carbon atom with respect to graphene, CC bond lengths, and CCC bond angles. Because of very high relative energies with respect to graphene (206–253 kJ mol$^{-1}$), the wavy-carbons may behave as energy reserving materials.



## 1. Introduction

Carbon is a familiar chemical element, which forms several types of allotropes, such as graphite, diamond, fullerenes [1], carbon nanotubes [2], and graphenes [3]. In addition to these well-known carbons, quantum chemical calculations recently suggested the existence of carbon molecules categorized to another class, which is composed of prism-carbon structures [4–6]. Chemical and thermal stabilities of the new series of prism-carbon structures were investigated with the GRRM method [7–11].

One of the new carbons is a prism-$C_{2n}$ series ($n = 8$–10, 12, 14, 16, 18 and 20) [4]. This series adopts a prism structure with carbon atoms at the ($n \times 2$) vertexes of a prism composed of two polygon ($n$-membered) rings and $n$ four-membered rings on the side faces, which looks like a hamster wheel. The prism-$C_{2n}$ structures can connect to each other by facing at four-membered rings and spread to forming various sheet structures, called the prism-$C_{2n}$ sheets. This family adopts a double-layered structure, where the prism-$C_{2n}$ ($n = 6$, 8, and 12) units are arranged horizontally [5]. The third new family is called prism-$C_n$ tubes, adopting a similar shape to that of carbon nanotubes but being composed of four-membered rings instead of five/six-membered rings, namely, which are constructed by axially piling up $n$-membered carbon polygons ($n = 3$–8, 10, 12, 14, 16, 18, and 20) [6]. The prism carbon sheets and tubes are periodic systems composed of tetravalent carbon atoms mutually connected with CC single bonds of ca. 0.15–0.16 nm [5,6].

We focused on the condensed four-membered ring unit. The unit does not appear quite often in carbon/carbohydrate compounds, but there are some well-known molecules with condensed four-membered rings, such as prismanes and various polycyclic alkanes [12–15]. We assumed that there would be another series of carbon structures that take a four-membered ring as a key motif. We, therefore, have made further computational explorations for the possibility of carbon structures with the key motif. Here, we present a new family, wavy carbons, composed of periodic arrays of four-membered carbon rings.

## 2. Methods and calculations

All electronic state calculations in the present study were performed for the ground singlet states, by using a GAUSSIAN 09 program package [16].

* Corresponding author at: Department of Chemistry, Graduate School of Science, Tohoku University, Aramaki, Aoba-ku, Sendai 980-8578, Japan.
*E-mail address:* ohnok@m.tohoku.ac.jp (K. Ohno).

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### 2.1. Explorations of the wavy structures

The first explorations of the wavy structures were carried out for $C_{2n}H_4$. Starting from flat ladder forms of $C_{2n}H_4$ ($n$ = 3–20) with an initial distance of all CC bonds to be 0.14 nm, geometry optimizations were performed at the level of B3LYP/6-31G(d) by using a minimization option of the GRRM program [11]. It is noted that the geometry optimization by the GRRM program is highly precise, since its criterion of the convergence is defined to be very tight.

The explorations of wavy structures purely with carbon atoms (wavy-$C_{2n}$) were then performed for $n > 10$ at the level of B3LYP/6-31G(d) by using the minimization option of the GRRM program. The geometry optimization calculations were started from regular polygon prism structures with an initial distance of the CC bonds on the polygons and on the side faces to be 0.144 nm and 0.150 nm, respectively.

### 2.2. Periodic boundary condition calculations for the wavy structures

The periodic wavy carbon structures were optimized by using the Periodic Boundary Conditions (PBC) of Gaussian 09 [16]. To reduce computational demands and to avoid the difficulties of PBC calculations arising from large basis functions, all PBC optimizations were carried out at the level of RHF/STO-3G. We chose this level for the minimal-basis ab initio calculations in the present study, because we assume that this series of structures has the same trend as the previously studied prism-$C_{2n}$ [4] and prism carbon sheets [5], which do not show any substantial effect on the optimized CC bond connections by the different levels between RHF/STO-3G, RHF/3-21G, B3LYP/6-31G(d), B3LYP/6-311++(2d,2p), B3LYP/cc-pVDZ, and B3LYP/cc-pVTZ.

The initial structures of the periodic wavy structures were determined based on the results of $C_{2n}H_4$ and wavy-$C_{2n}$ described in Section 2.1 and of prism carbons in the previous studies [4–6]. Representative input data and optimized parameters of the present PBC calculations are described in Supporting Information.

Wavy-$C_n$ sheets ($n$ = 2, 6, and 8) were produced by two-dimensional PBC (2D-PBC) energy-minimization calculations. One translational vector (Tv1) is along the wave direction of carbon chains including the $C_n$ unit, and the other translational vector (Tv2) is along the straight arrays of edges of the rectangular four-membered rings. The initial length of Tv2 was wholly set to be 0.160 nm, which was referred to a typical CC distance between the adjacent polygons in prism-$C_n$ tubes. The initial lengths of Tv1 were set to be longer with increasing the number of atoms employed in the wave unit. The wavy-$C_2$ sheet means that a sheet with a unit cell consisting of two C atoms. In this case, C atoms along the wave direction are arranged to be an up-down form. The initial geometries of the wavy-$C_2$ sheet were determined by a manner as what follows: The distance of the neighboring C atoms was set to be 0.160 nm, and the angle of three adjacent C atoms was set to be $\pm 120^\circ$ with the opposite sign between the neighbors as (−)(+) and so on. Thus the initial length of the Tv1 was set to be $0.160 \times 3^{1/2} = 0.27713$ nm. The initial geometries of the wavy-$C_6$ sheet, consisting of six atoms in the unit cell, were determined by a manner as what follows: The distance of the neighboring C atoms was set to be 0.160 nm, and the angle of three adjacent C atoms was set to be 120° with the ordering of signs to be (−)(−)(−)(+)(+)(+). The initial length of the Tv1 for the wavy-$C_6$ sheet was set to be $0.160 \times 3^{1/2} \times 2 = 0.55426$ nm. The initial geometries of the wavy-$C_8$ sheet, including eight atoms in the unit cell, were determined in a manner as what follows: The distance of the neighboring C atoms was set to be 0.160 nm, and the angle of three adjacent C atoms was set to be 135° with the ordering of signs to be (−)(−)(−)(−)(+)(+)(+)(+). The initial length of the Tv1 for the wavy-$C_8$ sheet was set to be $0.160 \times (2^{1/2} + 1) \times 2 = 0.77255$ nm.

A wavy-$C_{36}$ tube was produced by one-dimensional PBC (1D-PBC) energy-minimization calculations based on the wavy-$C_{36}$ obtained by the calculations in Section 2.1. The initial translational vector along the tube axis was set to be 0.160 nm.

## 3. Results and discussion

### 3.1. Explored wavy carbon structures

The geometry optimizations starting from the flat ladder forms of $C_{2n}H_4$ ($n$ = 3–20) gave various ladder-type structures. When the size was up to $n$ = 8 ($C_{16}H_4$), we found that the ladder adopted a wavy form **1** (Figure 1a). We noted that this $C_{2h}$ structure of $C_{16}H_4$ clearly shows an interesting nature of a carbon ladder that it preferentially adopts a wavy form in larger systems. Thus, we have investigated the structures by increasing the size up to $n$ = 20, until obtaining a remarkably waving $C_{40}H_4$ **2** (Figure 1b). After

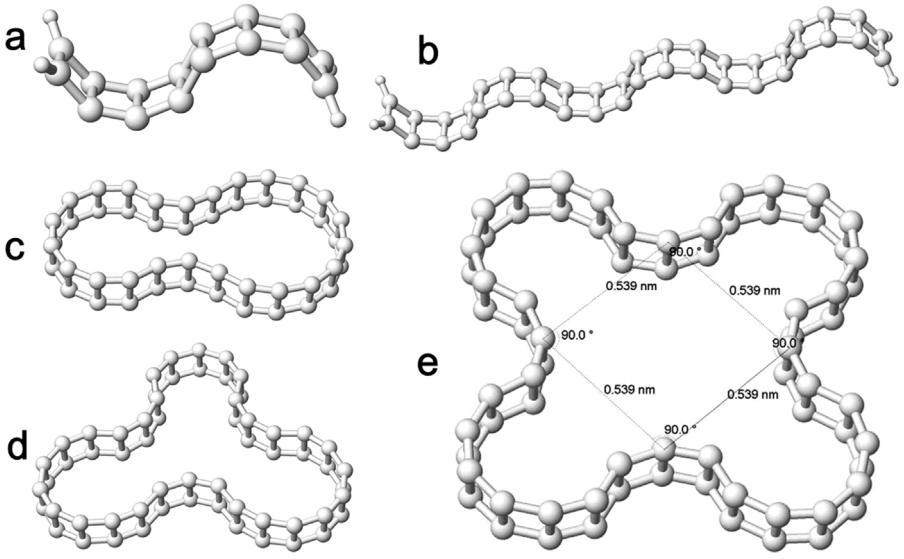


**Figure 1.** Various wavy forms of $C_{2n}H_4$ and $C_{2n}$ optimized at the level of B3LYP/6-31G(d). (a) $C_{16}H_4$(**1**), (b) $C_{40}H_4$(**2**), (c) $C_{48}$(**3**), (d) $C_{60}$(**4**), and (e) $C_{72}$(**5**).