#### Carbon 171 (2021) 96-103

Contents lists available at ScienceDirect

## Carbon

journal homepage: www.elsevier.com/locate/carbon

### **Research Article**

# Cyclo[18]carbon as an ultra-elastic molecular O-ring with unique mechanical properties

## Siyuan Fang , Yun Hang Hu

Department of Materials Science and Engineering, Michigan Technological University, Houghton, MI, 49931-1295, United States

#### ARTICLE INFO

Article history Received 10 August 2020 Received in revised form 28 August 2020 Accepted 31 August 2020 Available online 3 September 2020

Keywords: Cyclo[18]carbon Mechanical properties Tension Expansion Energy gap

#### ABSTRACT

Recent atomic manipulation by an AFM tip created the first sp-hybridized carbon material - cyclo[18] carbon. Herein, we revealed the unique mechanical properties of cyclo[18]carbon by the first principle calculations. Under uniaxial tension, cyclo[18]carbon is ultra-elastic as demonstrated by a small Young's modulus of 0.11 TPa and a tiny specific tensile stiffness of  $7.0 \times 10^6$  N m/kg, which are one and two orders of magnitude smaller than those of other carbon materials, respectively. The expansion and contraction of cyclo[18] carbon exhibit a relatively high specific stiffness of  $9.95 \times 10^8$  N m/kg, and it would be broken with an energy requirement of 34.14 eV. While uniaxial tension enables the insulator-semiconductor transition of cyclo[18]carbon, expansion enlarges its energy gap. Furthermore, the strain energy was proposed as a function of bond angle and bond length for uniaxially-stretched and expanded/contracted cyclo[18]carbon respectively, which sheds light on predicting the mechanical properties of certain materials. The unique properties of cyclo[18]carbon are of great interest for its potential use as an ultraelastic molecular O-ring in nanomechanical system and molecular electronics and devices.

© 2020 Elsevier Ltd. All rights reserved.

#### 1. Introduction

The last thirty years have witnessed an ongoing series of amazing breakthroughs in carbon allotropes which play a leading role in the modern science and technology [1-3]. The sp<sup>2</sup>-hybridized carbons (C60, carbon nanotube, and graphene) have been widely and thoroughly investigated while the sp-hybridized ones still remain as a mysterious member in the carbon family.

As early as 1921, sp-hybridized carbon chain (carbyne) was first proposed by Tammann [4]. Since then, a great number of theoretical and experimental studies have been conducted, whereas no one can provide direct evidence of the structure and properties of sp-hybridized carbon. In 2019, Kaiser et al. accomplished the in-situ synthesis and imaging of cyclo[18]carbon via atom manipulation by an AFM tip at 5 K [5]. This is the first time that the sp-hybridized carbon material was created, and more importantly, the polyynic structure was demonstrated. The authors also revealed that a modified Heyd-Scuseria-Ernzerhof (HSE) hybrid functional with an exact change ratio of 0.8 could accurately predict the geometric structure of cyclo[18]carbon [5], which is an important reference for theoretical calculations of sp-hybridized carbon materials.

Stimulated by this excellent work, the nature of the observed structure of cyclo[18]carbon was revealed, together with a variety of calculation methods being evaluated [6-10]. More importantly, a number of interesting properties of cyclo[18]carbon have been theoretically proposed [11-15]. For example, Stasyuk et al. predicted cyclo[18]carbon as the smallest all-carbon electron acceptor [11], while Zhang et al. reported its diverse electron transport properties when it is connected to carbon chain, graphene and 3D silver electrodes [12]. Besides, Kozuch and coworkers revealed an extremely rapid heavy atom tunneling in the gas-phase automerization process of cyclo[18]carbon [13]. Moreover, Boldyrev and coworkers indicated that the aromaticity of cyclo[18]carbon can be used for kinetic trapping with an estimated barrier of 30 kcal/mol [14]. So far, most studies on cyclo[18]carbon focus on its structure transformation, electron transport, molecule vibration, magnetism, and aromaticity. However, the mechanical properties of cyclo[18] carbon, which are of vital importance for its practical applications, have not been explored yet.

In this work, we employed the first principle calculations with a modified HSE method to evaluate the mechanical properties of cyclo[18]carbon as well as its geometric and electronic structure change during mechanical deformation such as tension, expansion and contraction. These unique properties reveal that cyclo[18]





Carb



Corresponding author. E-mail address: yunhangh@mtu.edu (Y.H. Hu).

carbon can be applied as an ultra-elastic molecular O-ring with tunable energy gaps in nanomechanical system and molecular electronics and devices.

#### 2. Calculation method

The electronic structure of cyclo[18]carbon was calculated using DFT implemented in Gaussian 16 package [16]. The Heyd-Scuseria-Ernzerhof hybrid functional (HSE03) [17] was employed with its fraction of exact exchange set as 0.8. Similar modification of the functional has also been reported by Kaiser et al. [5], Pereira et al. [18], and Atalla et al. [19] Combined with def2-TZVP basis set [20,21], this modified functional could accurately predict the geometric structure of cyclo[18]carbon, which is in excellent agreement with the experimental result reported by Kaiser et al. [5] This calculation method could provide reliable HOMO-LUMO energy gaps as well [19], since it predicted an energy gap of 1.848 eV for C60, consistent with the experimental value (~1.8 eV) [22-24]. The electronic structure was analyzed with Multiwfn 3.7 (dev) code [25]. To perform uniaxial tension, the geometry of cyclo[18]carbon was optimized with fixing the distance between the first and tenth carbon atoms at a value larger than the original diameter (Fig. 1a, red arrows). All the other structure parameters are allowed to change during optimization. To evaluate expansion and contraction, cyclo[18]carbon optimization was carried out with the radius (the distance between the center and each carbon atom) fixed and other structure parameters being able to change (Fig. 1a, purple arrows). Expansion and contraction can be regarded as multiaxial tension and compression, respectively. To reach the convergence, the values of maximum force, RMS force, maximum displacement and RMS displacement must be lower than 0.00045, 0.00030, 0.00180 and 0.00120, respectively. The frequencies are calculated as well to find the deformation strength. Carbon atoms have been numbered as denoted in Fig. 1a, while bond  $n(B_n)$  is defined as the bond between  $C_n$  and  $C_{n+1}$ , and angle  $n(A_n)$  is defined as the angle among  $C_{n-1}$ ,  $C_n$ , and  $C_{n+1}$ . Logarithmic strain is used for all cases.

#### 3. Results and discussion

#### 3.1. Cyclo[18]carbon under uniaxial tension

The performance of cyclo[18]carbon under uniaxial tension is an important aspect to evaluate its mechanical properties. To perform uniaxial tension, the geometry of cyclo[18]carbon was optimized

with fixing the distance between the first and tenth carbon atoms at a value larger than the original diameter (as shown in Fig. 1a, red arrows). The optimized geometric structures of uniaxiallystretched cyclo[18]carbons are shown in Fig. 1b-g, in which the vertical symmetry of the structure and the bond length alternation are well maintained (Fig. 2a). Furthermore, by analyzing the relative change of the length of each bond (Fig. 2b), it is observed: (1) bonds near the tensile points (B<sub>1</sub>, B<sub>9</sub>, B<sub>10</sub> and B<sub>18</sub>) are stretched more than the distant ones, and (2) long bonds (even-numbered bonds) are stretched more than short bonds (odd-numbered bonds). Bond angles change with tensile strain as well (Fig. 2c), which makes cyclocarbon distinguish from carbyne. The bond angles at the tensile points  $(A_1 \text{ and } A_{10})$  significantly decrease while those away from the tensile points are even enlarged (Fig. 2d), indicating that keeping partial linear structure is energetically favorable under tension. Moreover, the relative change of bond angles is more significant than that of bond lengths, which means bond angle adjustment is more favorable to adapt to the tensile deformation. Above observations agree well with the results of stretching cyclo[18]carbon at different pairs of carbon atoms (e.g., the first-sixth pair and the first-eighth pair, see Figs. S1 and S2 for detailed results).

The HOMO-LUMO energy gap of cyclo[18]carbon is 5.54 eV, in good agreement with the values reported by other groups [11,26]. The density-of-state (DOS) diagram and isosurface plots of HOMO and LUMO are shown in Figs. S3 and S4, from which we can observe that HOMO and LUMO are made of  $\pi$ -orbitals extending in the radial direction and locating perpendicular to the molecular plane. respectively. It is interesting that the HOMO-LUMO energy gap decreases with strain, and even reaches 3.73 eV at a strain of 32% (Fig. 1). The narrowed energy gap is mainly resulted by the downshift of LUMO which is composed of in-plane  $\pi$ -orbitals (Figs. S3 and S4). Here, uniaxial tension enables the insulatorsemiconductor transition for cyclo[18]carbon. This is totally different from carbyne, which shows a mechanically induced metal-insulator transition due to the Peierls distortion [27,28]. The different electronic properties of carbon chains and carbon rings broaden the potential application areas of emerging sp-hybridized carbon materials.

To further evaluate the tensile properties of cyclo[18]carbon, the specific tensile stiffness (k), tensile stiffness ( $k_Y$ ), and Young's modulus (Y) are calculated, which are defined as [28–30]:



**Fig. 1.** Schematic method and geometric structure of cyclo[18]carbons under uniaxial tension. (a) Schematic method for uniaxial tension and expansion/contraction of cyclo[18] carbon. (b)–(g) Geometric structure and HOMO-LUMO energy gap of cyclo[18]carbons under uniaxial tension.  $\varepsilon$  and  $E_{gap}$  stand for the strain and the HOMO-LUMO energy gap of cyclo[18]carbons under uniaxial tension.  $\varepsilon$  and  $E_{gap}$  stand for the strain and the HOMO-LUMO energy gap of cyclo[18]carbons under uniaxial tension.



**Fig. 2.** Bond properties, strain energy and pulling force of uniaxially stretched cyclo[18]carbons. (a) Bond length of stretched cyclo[18]carbons (B<sub>n</sub> is defined as the bond between C<sub>n</sub> and C<sub>n+1</sub>). (b) Relative change of bond length of stretched cyclo[18]carbons. (c) Bond angle of stretched cyclo[18]carbons (A<sub>n</sub> is defined as the angle among C<sub>n-1</sub>, C<sub>n</sub>, and C<sub>n+1</sub>). (d) Relative change of bond angle of stretched cyclo[18]carbons. (e) Strain energy as a function of strain, fitted with a fourth-order polynomial ( $R^2 = 0.99998$ ). (f) Pulling force obtained from the first derivative of the fitted strain energy-strain curve ( $F = \frac{\partial E_{i}}{\partial c_{i} k_{i}}$ ).

$$k = \frac{\partial^2 E_s}{\partial \varepsilon^2} |_{\varepsilon = 0} \tag{1}$$

$$k_{\rm Y} = \frac{k}{d} \tag{2}$$

$$Y = \frac{k_Y}{S} \tag{3}$$

where  $E_s$ ,  $\varepsilon$ , d, and S are the strain energy, strain, diameter of unstretched cyclo[18]carbon (7.3038 Å), and effective cross-sectional area, respectively. By fitting our data (strain energy as a function of strain) with a fourth-order polynomial (Fig. 2e) [28], the specific tensile stiffness is demonstrated as 7.0 × 10<sup>6</sup> N m/kg, which is two orders of magnitude smaller than those of carbyne [28], graphene [31–34], carbon nanotube [35,36], and diamond (Table 1) [37]. Corresponding tensile stiffness is then determined to be 3.43 nN (for one cyclo[18]carbon molecule). To calculate Young's modulus, the diameter of the effective cross section is assumed to be 2 Å based on the electron density distribution in the C–C bond [29,30]. This value has been widely used for carbon chains [38–41], and has also been supported by the electronic structure of cyclo[18]carbon [6,8,10]. Thus, in this case, Young's modulus is estimated to be 0.11 TPa, again much smaller than those of carbyne (32.71 TPa) [28], graphene (1 Tpa) [33], carbon nanotube (1.8 Tpa) [42], and diamond (1.2 TPa) [43].

Tensile strength is another vital metric of engineering materials, which can be theoretically predicted by calculating the number of imaginary frequencies [28,34]. For stretched cyclo[18]carbon, imaginary frequency appears at a strain of 32% (vibration along the tension direction, see Table S1 for details), with a pulling force of

| material        | specific stiffness (N·m/kg) | Young's modulus (TPa) | specific strength (N $\cdot$ m/kg) | critical strain | critical force (nN) | Ref.             |
|-----------------|-----------------------------|-----------------------|------------------------------------|-----------------|---------------------|------------------|
| cyclo[18]carbon | $7.0 \times 10^{6}$         | 0.11                  | $5.0 \times 10^7$                  | 32%             | 4.5                 | This work        |
| carbyne         | $1.0 \times 10^9$           | 32.7                  | $6.0-7.5 	imes 10^{7}$             | 18%             | 11.7                | [28,44,45]       |
| carbon nanotube | $4.5 \times 10^8$           | 1.8                   | $4.3 - 5.0 	imes 10^7$             | -               | -                   | [35,36,42,46,47] |
| graphene        | $4.5 - 9.7 \times 10^{8}$   | 1                     | $4.7 - 5.5 	imes 10^7$             | -               | -                   | [31-34]          |
| diamond         | $3.5 \times 10^{8}$         | 1.2                   | $2.5 - 6.5 \times 10^7$            | -               | -                   | [37,43,48]       |

 Table 1

 Comparation of tensile properties of carbon materials.

4.5 nN (Fig. 2f). In contrast, as reported by Yakobson and coworkers, the critical strain of carbyne is 18% at 11.7 nN [28], indicating that carbon ring is more elastic than carbon chain. The specific tensile strength of cyclo[18]carbon is then estimated to be  $5.0 \times 10^7$  N m/kg, similar to those of other carbon materials (2.5–7.5 × 10<sup>7</sup> N m/kg, shown in Table 1). In addition, only when the strain exceeds ~50% can the ring structure of cyclo[18]carbon be destroyed. Namely, the ultimate elongation of cyclo[18]carbon is ~50%. The above-discussed tiny tensile stiffness and decent tensile strength of cyclo[18]carbon together with its tunable energy gap enable it to perform as an ultra-elastic molecular O-ring with promising applications in nanomechanical system and molecular electronics and devices.

Via comparing the tensile properties of various carbon materials (Table 1), it is very interesting to find that while carbyne is predicted as the strongest nanomaterial [28], cyclocarbon is considered to be ultra-elastic, though both of them are composed of sphybridized carbon atoms. The reason is, as mentioned above, both bond length and bond angle can be tuned when stretching a cyclocarbon molecule, making it more liable to adapt to deformation, while only bond length can be changed for a stretched carbyne. As for other carbon materials (e.g., carbon nanotube, graphene, and diamond), the sp<sup>2</sup>-hybridized hexagonal network and the  $sp^3$ -hybridized tetrahedral structure also enable the change of bond angles under tension, while their elasticities are limited by the abundance of composing carbon atoms. This is why their tensile properties fall in between those of cyclocarbon and carbyne. Furthermore, compared with stretching a bond which will lead to a significant increase of the bond energy, tuning the bond angle is more likely to happen. This has been demonstrated in Fig. 2a-d and also in our previous work that the atomic carbon chain would be bent instead of being compressed when fixing the distance between the end carbon atoms (shorter than the original one) [24]. These observations provide some insights into the prediction of the mechanical properties of certain materials.

#### 3.2. Cyclo[18]carbon during expansion and contraction

Given the high elasticity of cyclo[18]carbon, it is highly desirable to further investigate how it would behave during expansion and contraction (as shown in Fig. 1a, purple arrows). The optimized geometric structures of expanded/contracted cyclo[18]carbons with different radii (Fig. S5) demonstrate the evident change in bond lengths and negligible change in bond angles (fixed at  $\sim 160^{\circ}$ ). Owing to the high symmetry, the bond lengths of expanded/contracted cyclo[18]carbon are in a repeating manner, just as that of the original cyclo[18]carbon. Bond length alternation is maintained as long as the expansion/contraction degree  $\left(\frac{R-R_0}{R_0}\right)$  is above -9.6%, while polyyne-cumulene transition can be induced by further compression (Fig. 3a). This happens because the longer bond is compressed more due to its less electron distribution while the shorter bond is compressed less due to the relatively abundant electron distribution. As a result, the bond length eventually becomes uniform under compression. Moreover, during expansion, long bonds are also more liable to be deformed, consistent with the case under uniaxial tension. When the expansion degree reaches 26.0%, the continuous structure of cyclo[18]carbon is destroyed, and further expansion gradually breaks cyclo[18]carbon into 2, 3, 4, and 6 parts (Fig. S6). The energies of expanded/contracted cyclo[18] carbons are shown in Fig. 3b. An energy drop is observed at the breaking point, by which can we speculate the energy requirement for breaking cyclo[18]carbon. Namely, although the energy difference between the original and the broken cyclo[18]carbons is just 14.66 eV, a much higher energy of 34.14 eV is required to break cyclo[18]carbon (inset Fig. 3b).

The HOMO-LUMO energy gap changes with the expansion/ contraction degree of cyclo[18]carbon (Fig. 3c). The smallest energy gap (4.80 eV) is achieved at a 9.6% contraction while the largest one (7.66 eV) is obtained at a 16.4% expansion. For expanded cyclo[18] carbon (16.4% expansion), both HOMO and LUMO shift to lowenergy states (Fig. S3). Moreover, though the composition of HOMO and LUMO is similar to that of undeformed cyclo[18]carbon, the electron distribution in the LUMO of expanded cyclo[18]carbon is more uniform (Fig. S4). Here, the expansion of cyclo[18]carbon always generates a larger energy gap than the original one, which can be utilized as a novel approach to enlarge the energy gap (which cannot be achieved via uniaxial tension).

The expansion/contraction rigidity of cyclo[18]carbon is further investigated. Herein, expansion/contraction is regarded as multiaxial tension. Similar to the above-discussed uniaxial tension, the strain energy-strain curve under expansion/contraction is also fitted with a fourth-order polynomial (Fig. 3d). A high specific expansion/contraction stiffness of 9.95  $\times$  10<sup>8</sup> N m/kg is then obtained with Eq. (1), which indicates it is much harder to perform expansion and contraction for cyclo[18]carbon compared with uniaxial tension (a 143-fold enhancement in the specific stiffness). This is because, in this condition, the bond angles are almost fixed (at  $\sim 160^{\circ}$ ) and the only approach to adapt to the deformation is to elongate the bonds, which would place cyclo[18]carbon in a much higher energy state than the original one (without deformation). This scenario is very similar to stretching carbyne, thus leading to the similar specific stiffnesses  $(9.95 \times 10^8 \text{ vs.} 1 \times 10^9 \text{ N m/kg})$  [28]. It can be speculated that if cyclo[18]carbon is set on/in a rigid molecular cylinder (e.g., carbon nanotube), its shape is defined and additional stresses arise. Moreover, there may exist extra stabilization of such a promising composite due to confinement as well. Nevertheless, this specific stiffness is still in the same order of magnitude as the specific tensile stiffnesses of other carbon materials (Table 1) [31-37], which indicates the promising application of cyclo[18]carbon as an elastic molecular O-ring.

#### 3.3. Effects of bonding strength on mechanical properties

The reason for the unique mechanical properties of cyclo[18] carbon is further analyzed from the perspective of bonding. The total bonding strength (BS) can be divided into two components: orientation-dependent one  $(BS_d)$  and orientation-independent one  $(BS_{nd})$ .



**Fig. 3.** Structure, energy, and property of expanded/contracted cyclo[18]carbons. (a) Bond length of adjacent carbon atoms in expanded/contracted cyclo[18]carbons (length 1 and length 2 are defined as the lengths of B<sub>n</sub> with n as odd and even numbers, respectively). (b) Energy of expanded/contracted cyclo[18]carbons (inset: schematic energy requirement for breaking cyclo[18]carbon). (c) HOMO-LUMO energy gap of expanded/contracted cyclo[18]carbons. (d) Strain energy-strain curve fitted with a fourth-order polynomial ( $R^2 = 1$ ). The expansion/contraction degree is defined as  $\frac{R_{-R_0}}{R_0}$  with positive and negative values for expansion and contraction, respectively.

 $BS = BS_d + BS_{nd} \tag{4}$ 

Since covalent bonding requires the match in both orbital orientations and energies, its strength is highly dependent on the bond angle [49]. For sp-hybridized carbon, the perfect bond angle is  $180^{\circ}$  and any deviation will cause the strain [24]. The strength of orientation-dependent bonding of sp-hybridized carbon is equal to the projection of that at the perfect orientation (BS<sub>dp</sub>).

$$BS_d = \sum_{i=1}^n \left( BS_{dp} \times \sin\frac{\theta_i}{2} \right) \tag{5}$$

in which  $\theta$  is the bond angle. The orientation-independent bonding strength can be expressed by the interatomic potential using the Tersoff model [50,51]:

$$BS_{nd} = \frac{1}{2} \sum_{i} \left( \sum_{j \neq i} V_{ij} \right) \tag{6}$$

where  $V_{ij}$  is the analytical form of the pair potential. Then the total bonding strength can be obtained by combing Eq. (5) and Eq. (6):

$$BS = \sum_{i=1}^{n} \left( BS_{dp} \times sin\frac{\theta_i}{2} \right) + \frac{1}{2} \sum_{i} \left( \sum_{j \neq i} V_{ij} \right)$$
(7)

Under uniaxial tension, the change of bond angles is resulted at all carbon atoms, while the change of bond lengths is not obvious as long as it is not being stretched to a linear molecule. In this case, the strain energy  $(E_s)$  should be equal to the change of total bonding strength due to the bond angle adjustment:

$$E_{s} = \Delta BS = BS_{dp} \times \sum_{i=1}^{18} \left( \sin \frac{\theta_{0}}{2} - \sin \frac{\theta_{i}}{2} \right)$$
(8)

where i is the ordinal number of carbon.  $\theta_0$  and  $\theta_i$  are bond angles of the original and uniaxially-stretched cyclo[18]carbon. As shown in Fig. 4a, a good linear relationship ( $R^2=0.9937$ ) is observed between the strain energy ( $E_s$ ) and  $\sum_{i=1}^{18} \left( sin \frac{\theta_0}{2} - sin \frac{\theta_i}{2} \right)$ . Thus, the following linear equation can be obtained:



Fig. 4. Strain energy as a function of bond parameters. (a) Strain energy as a function of bond angles for uniaxially-stretched cyclo[18]carbon. (b) Strain energy as a function of bond lengths for expanded/contracted cyclo[18]carbon.

$$E_{s} = 9.7114 \times \sum_{i=1}^{18} \left( 0.9848 - \sin\frac{\theta_{i}}{2} \right)$$
(9)

by which the strain energy can be easily calculated from bond angles for any uniaxially-stretched cyclo[18]carbon. This methodology can be further generalized into other sp-hybridized carbon materials.

In contrast, for expanded/contracted cyclo[18]carbon, the change of bond angles is negligible while the change of bond lengths is significant. Therefore, here, the change of total bonding strength is simplified as:

$$\Delta BS = \Delta BS_{nd} = \Delta \left[ \frac{1}{2} \sum_{i} \left( \sum_{j \neq i} V_{ij} \right) \right]$$
(10)

where V<sub>ii</sub> can be calculated via:

$$V_{ij} = f_C(r_{ij}) \times (a_{ij} \times A \times e^{-\lambda_1 \times r_{ij}} - b_{ij} \times B \times e^{-\lambda_2 \times r_{ij}})$$
(11)

in which  $r_{ij}$  is the distance between the ith and jth atoms.  $f_C(r)$  is a cutoff term ensuring only nearest-neighbor interactions, which is equal to 1,  $\frac{1}{2} - \frac{1}{2} \sin \left[ \frac{\pi(r_{ij}-1.95)}{0.3} \right]$ , and 0 when  $r_{ij} \leq 1.8$  Å, 1.8 Å <  $r_{ij} \leq 2.1$  Å, and  $r_{ij} > 2.1$  Å, respectively [50].  $a_{ij}$  is a range-limiting term (typically set as 1) [52], while  $b_{ij}$  is a bond order term. A, B,  $\lambda_1$  and  $\lambda_2$  are all constants, equal to 1393.6 eV, 346.74 eV, 3.4879 Å<sup>-1</sup>, and 2.2119 Å<sup>-1</sup>, respectively [50,52]. For cyclo[18]carbon, most  $f_C(r)$  is equal to either 0 or 1, thereby it is reasonable to simplify the function by considering interatomic potentials of the nearest carbon pairs only. Moreover, since  $b_{ij}$  is directly related to the bond angle [52] that does not change during expansion/contraction, we regard  $b_{ij}$  as a constant (b). Thus, based on the Tersoff model as described in Eq. (6) and Eq. (11), we propose a function of the change of the total bonding strength in terms of bond lengths of expanded/contracted cyclo[18]carbon:

$$\Delta BS = \Delta \sum_{i=1}^{18} \left( 1393.6e^{-3.4879L_i} - b \times 346.74e^{-2.2119L_i} \right)$$
(12)

where L<sub>i</sub> is the bond length between adjacent carbon atoms. Then, by fitting the data of strain energies and considering the bonding strength of undeformed cyclo[18]carbon, the following function is obtained:

$$E_{s} = \Delta BS = \sum_{i=1}^{18} \left( 1393.6e^{-3.4879L_{i}} - 417.7e^{-2.2119L_{i}} \right) + 150.02$$
(13)

where the constant term (150.02) corresponds to the bonding strength of undeformed cyclo[18]carbon. As shown in Fig. 4b, the calculated strain energies agree perfectly with the observed ones ( $R^2 = 0.9988$ ). Thus, via Eq. (13), we can accurately predict the strain energy based on bond lengths of expanded/contracted cyclo [18]carbon. More importantly, this is a good example for predicting the mechanical properties of materials with only bond lengths being able to be changed.

#### 4. Conclusion

In conclusion, the first principle calculations demonstrated that cyclo[18]carbon can perform as an ultra-elastic molecular O-ring with tunable energy gap. Cyclo[18]carbon has a small Young's modulus of 0.11 TPa and a tiny specific tensile stiffness of  $7.0 \times 10^6$  N m/kg, which are one and two orders of magnitude lower than those of other carbon materials. The critical strain of cyclo[18] carbon is 32% at a pulling force of 4.5 nN, indicating its ultra-elastic property compared with carbyne due to the change of bond angles. Moreover, the specific expansion/contraction stiffness of cyclo[18] carbon is estimated to be  $9.95 \times 10^8$  N m/kg, and its continuous structure is destroyed at a 26% expansion with an energy requirement of 34.14 eV. Additionally, it was demonstrated that uniaxial tension enables the insulator-semiconductor transition of cyclo[18] carbon while expansion can enlarge the energy gap of cyclo[18]

carbon. Furthermore, the strain energy was revealed as a function of bond angle for uniaxially-stretched cyclo[18]carbon and a function of bond length for expanded/contracted cyclo[18]carbon. The unusual elasticity of cyclo[18]carbon together with its tunable energy gap suggests that cyclo[18]carbon is able to serve as an ultra-elastic molecular O-ring with promising applications in nanomechanical system as well as molecular electronics and devices. To make it come true, lifetime enhancement study and further investigations into its electronic properties are highly desirable.

#### **CRediT** authorship contribution statement

**Siyuan Fang:** Investigation, Writing - original draft. **Yun Hang Hu:** Conceptualization, Supervision, Writing - review & editing.

#### **Declaration of competing interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Acknowledgements

We are grateful for support from National Science Foundation (CMMI-1661699) and ACS Petroleum Research Fund (PRF-60329-ND10).

#### Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.carbon.2020.08.082.

#### References

- H.W. Kroto, J.R. Heath, S.C. O'Brien, R.F. Curl, R.E. Smalley, C60: buckminsterfullerene, Nature 318 (1985) 162–163.
- [2] S. lijima, Helical microtubules of graphitic carbon, Nature 354 (1991) 56–58.
   [3] K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, Y. Zhang, S.V. Dubonos,
- [3] K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, Y. Zhang, S.V. Dubonos, I.V. Grigorieva, A.A. Firsov, Electric field effect in atomically thin carbon films, Science 306 (2004) 666.
- [4] G. Tammann, Carbon formed by the action of mercury on carbon tetrachloride, carbon tetrabromide, and carbon tetraiodide, Zeitschrift fuer Anorganische und Allgemeine Chemie 115 (1921) 145–158.
- [5] K. Kaiser, L.M. Scriven, F. Schulz, P. Gawel, L. Gross, H.L. Anderson, An sphybridized molecular carbon allotrope, cyclo[18]carbon, Science 365 (2019) 1299.
- [6] Z. Liu, T. Lu, Q. Chen, An sp-hybridized all-carboatomic ring, cyclo[18]carbon: electronic structure, electronic spectrum, and optical nonlinearity, Carbon 165 (2020) 461–467.
- [7] Z. Liu, T. Lu, Q. Chen, An sp-hybridized all-carboatomic ring, cyclo[18]carbon: bonding character, electron delocalization, and aromaticity, Carbon 165 (2020) 468–475.
- [8] B. Shi, L. Yuan, T. Tang, Y. Yuan, Y. Tang, Study on electronic structure and excitation characteristics of cyclo[18]carbon, Chem. Phys. Lett. 741 (2020) 136975.
- [9] É. Brémond, Á.J. Pérez-Jiménez, C. Adamo, J.C. Sancho-García, sp-hybridized carbon allotrope molecular structures: an ongoing challenge for densityfunctional approximations, J. Chem. Phys. 151 (2019) 211104.
- [10] G.V. Baryshnikov, R.R. Valiev, A.V. Kuklin, D. Sundholm, H. Ågren, Cyclo[18] carbon: insight into electronic structure, aromaticity, and surface coupling, J. Phys. Chem. Lett. 10 (2019) 6701–6705.
- [11] A.J. Stasyuk, O.A. Stasyuk, M. Solà, A.A. Voityuk, Cyclo[18]carbon: the smallest all-carbon electron acceptor, Chem. Commun. 56 (2020) 352–355.
- [12] L. Zhang, H. Li, Y.P. Feng, L. Shen, Diverse transport behaviors in cyclo[18] carbon-based molecular devices, J. Phys. Chem. Lett. 11 (2020) 2611–2617.
- [13] A. Nandi, E. Solel, S. Kozuch, Carbon tunneling in the automerization of cyclo [18]carbon, Chem. Eur J. 26 (2020) 625–628.
- [14] N. Fedik, M. Kulichenko, D. Steglenko, A.I. Boldyrev, Can aromaticity be a kinetic trap? Example of mechanically interlocked aromatic [2-5]catenanes built from cyclo[18]carbon, Chem. Commun. 56 (2020) 2711–2714.
- [15] N.D. Charistos, A. Muñoz-Castro, Induced magnetic field in sp-hybridized carbon rings: analysis of double aromaticity and antiaromaticity in cyclo [2N]carbon allotropes, Phys. Chem. Chem. Phys. 22 (2020) 9240–9249.

- [16] M. Frisch, G. Trucks, H. Schlegel, G. Scuseria, M. Robb, J. Cheeseman, G. Scalmani, V. Barone, G. Petersson, H. Nakatsuji, Gaussian 16, Revision a. 03, Gaussian Inc., 2016.
- [17] J. Heyd, G.E. Scuseria, M. Ernzerhof, Hybrid functionals based on a screened Coulomb potential, J. Chem. Phys. 118 (2003) 8207–8215.
- [18] Z.S. Pereira, E.Z. da Silva, Spontaneous symmetry breaking in cyclo[18]Carbon, J. Phys. Chem. 124 (2020) 1152–1157.
- [19] V. Atalla, M. Yoon, F. Caruso, P. Rinke, M. Scheffler, Hybrid density functional theory meets quasiparticle calculations: a consistent electronic structure approach, Phys. Rev. B 88 (2013) 165122.
- [20] F. Weigend, Accurate Coulomb-fitting basis sets for H to Rn, Phys. Chem. Chem. Phys. 8 (2006) 1057–1065.
- [21] F. Weigend, R. Ahlrichs, Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: design and assessment of accuracy, Phys. Chem. Chem. Phys. 7 (2005) 3297–3305.
- [22] Y.I. Prylutskyy, S.S. Durov, L.A. Bulavin, I.I. Adamenko, K.O. Moroz, I.I. Geru, I.N. Dihor, P. Schaff, P.C. Eklund, L. Grigorian, Structure and thermophysical properties of fullerene C60 aqueous solutions, Int. J. Thermophys. 22 (2001) 943–956.
- [23] R. Rivelino, F. de Brito Mota, Band gap and density of states of the hydrated C60 fullerene system at finite temperature, Nano Lett. 7 (2007) 1526–1531.
- [24] Y.H. Hu, Bending effect of sp-hybridized carbon (carbyne) chains on their structures and properties, J. Phys. Chem. 115 (2011) 1843.
- [25] T. Lu, F. Chen, Multiwfn: a multifunctional wavefunction analyzer, J. Comput. Chem. 33 (2012) 580–592.
- [26] M. Li, Z. Gao, Y. Han, Y. Zhao, K. Yuan, S. Nagase, M. Ehara, X. Zhao, Potential molecular semiconductor devices: cyclo-Cn (n = 10 and 14) with higher stabilities and aromaticities than acknowledged cyclo-C18, Phys. Chem. Chem. Phys. 22 (2020) 4823–4831.
- [27] V.I. Artyukhov, M. Liu, B.I. Yakobson, Mechanically induced metal-insulator transition in carbyne, Nano Lett. 14 (2014) 4224–4229.
- [28] M. Liu, V.I. Artyukhov, H. Lee, F. Xu, B.I. Yakobson, Carbyne from first principles: chain of C atoms, a nanorod or a nanorope, ACS Nano 7 (2013) 10075–10082.
- [29] S. Kotrechko, I. Mikhailovskij, T. Mazilova, E. Sadanov, A. Timoshevskii, N. Stetsenko, Y. Matviychuk, Mechanical properties of carbyne: experiment and simulations, Nanoscale Res. Lett. 10 (2015) 24.
- [30] A. Timoshevskii, S. Kotrechko, Y. Matviychuk, Atomic structure and mechanical properties of carbyne, Phys. Rev. B 91 (2015) 245434.
- [31] R. Majidi, Density functional theory study on structural and mechanical properties of graphene, T-graphene, and R-graphyne, Theor. Chem. Acc. 136 (2017) 109.
- [32] L. Zhou, G. Cao, Nonlinear anisotropic deformation behavior of a graphene monolayer under uniaxial tension, Phys. Chem. Chem. Phys. 18 (2016) 1657–1664.
- [33] C. Lee, X. Wei, J.W. Kysar, J. Hone, Measurement of the elastic properties and intrinsic strength of monolayer graphene, Science 321 (2008) 385.
- [34] F. Liu, P. Ming, J. Li, Ab initio calculation of ideal strength and phonon instability of graphene under tension, Phys. Rev. B 76 (2007), 064120.
- [35] D. Sánchez-Portal, E. Artacho, J.M. Soler, A. Rubio, P. Ordejón, Ab initio structural, elastic, and vibrational properties of carbon nanotubes, Phys. Rev. B 59 (1999) 12678–12688.
- [36] D.H. Robertson, D.W. Brenner, J.W. Mintmire, Energetics of nanoscale graphitic tubules, Phys. Rev. B 45 (1992) 12592–12595.
- [37] K.E. Spear, J.P. Dismukes, Synthetic Diamond: Emerging CVD Science and Technology, John Wiley & Sons, 1994.
- [38] T.I. Mazilova, S. Kotrechko, E.V. Sadanov, V.A. Ksenofontov, I.M. Mikhailovskij, High-field Formation of Linear Carbon Chains and Atomic Clusters, 2010, pp. 151–157, 09.
- [39] X. Liu, G. Zhang, Y.-W. Zhang, Tunable mechanical and thermal properties of one-dimensional carbyne chain: phase transition and microscopic dynamics, J. Phys. Chem. C 119 (2015) 24156–24164.
- [40] G. Wu, J. Dong, Anomalous heat conduction in a carbon nanowire: molecular dynamics calculations, Phys. Rev. B 71 (2005) 115410.
- [41] B. Faria, C.E.S. Bernardes, N. Silvestre, J.N. Canongia Lopes, C13 a new empirical force field to characterize the mechanical behavior of carbyne chains, Phys. Chem. Chem. Phys. 22 (2020) 758–771.
- [42] M.M.J. Treacy, T.W. Ebbesen, J.M. Gibson, Exceptionally high Young's modulus observed for individual carbon nanotubes, Nature 381 (1996) 678–680.
- [43] L. Itzhaki, E. Altus, H. Basch, S. Hoz, Harder than diamond: determining the cross-sectional area and young's modulus of molecular rods, Angew. Chem. Int. Ed. 44 (2005) 7432–7435.
- [44] A.J. Kocsis, N.A.R. Yedama, S.W.J.N. Cranford, Confinement and controlling the effective compressive stiffness of carbyne, Nanotechnology 25 (2014) 335709.
- [45] C.S.W. Nair A K, M.J. Buehler, The minimal nanowire: mechanical properties of carbyne, Europhys. Lett. 95 (2011).
- [46] S. Ogata, Y. Shibutani, Ideal tensile strength and band gap of single-walled carbon nanotubes, Phys. Rev. B 68 (2003) 165409.
- [47] C.-C. Chang, I.K. Hsu, M. Aykol, W.-H. Hung, C.-C. Chen, S.B. Cronin, A new lower limit for the ultimate breaking strain of carbon nanotubes, ACS Nano 4 (2010) 5095–5100.
- [48] R.H. Telling, C.J. Pickard, M.C. Payne, J.E. Field, Theoretical strength and cleavage of diamond, Phys. Rev. Lett. 84 (2000) 5160–5163.
- [49] A.R. West, Solid State Chemistry and its Applications, John Wiley & Sons, 2014.

- [50] J. Tersoff, Empirical interatomic potential for carbon, with applications to amorphous carbon, Phys. Rev. Lett. 61 (1988) 2879–2882.
  [51] J. Tersoff, New empirical approach for the structure and energy of covalent systems, Phys. Rev. B 37 (1988) 6991–7000.
- [52] L. Lindsay, D.A. Broido, Optimized Tersoff and Brenner empirical potential parameters for lattice dynamics and phonon thermal transport in carbon nanotubes and graphene, Phys. Rev. B 81 (2010) 205441.