



ChemComm

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Journal:	<i>ChemComm</i>
Manuscript ID	CC-COM-09-2020-006373.R2
Article Type:	Communication

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## COMMUNICATION

## A theoretical study on the strain energy of helicene-containing carbon nanobelts

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Received 00th January 20xx,

Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

In this study, the theoretical analysis of the strain energy of helicene-containing carbon nanobelt is reported. It was found that the combined method of linear regression analysis and suitable homodesmotic reactions can successfully estimate the strain energies of various helicene-containing carbon nanobelts including previously synthesized chiral (18,12) carbon nanobelts.

Carbon nanobelts (CNBs), the sidewall segment molecules of carbon nanotubes (CNTs),<sup>1</sup> have attracted growing attention in recent years, owing to their radial  $\pi$ -conjugation, strain-induced reactivity<sup>2</sup> and potential applications in template CNT synthesis. Various CNB structures such as cyclacenes, cyclophenacenes and Vögtle belt have been proposed and investigated by both theoretical and synthetic organic chemists.<sup>3–12</sup> Recently, our group synthesized armchair-type  $(n,n)$ CNB ( $A_n$ ;  $n = 6, 8, 12$ ; Fig. 1a) and a zigzag-type (18,0)CNB.<sup>13–16</sup> A chiral-type (18,12)CNB with [4]helicene structures was synthesized by Chi, Miao and co-workers.<sup>17</sup> Apart from these known CNBs, other CNBs with more complex structures can also be designed by modulating the method for cutting the CNTs. CNBs with helicene structures ( $B_n$ – $E_n$ , Fig. 1b) are the representative examples of these complex structures, and the structural properties of such unexplored CNBs have been of interest.

To estimate the feasibility of synthesizing strained belt-shaped compounds, the calculation of strain energy (SE) is effective.<sup>18</sup> While homodesmotic reaction method<sup>19</sup> using reference molecules is generally used for strained molecules (e.g., cycloparaphenylenes),<sup>20</sup> we found that conventional homodesmotic reactions using small reference molecules could not be applied to CNBs because of the generation of negative SE values in some cases.<sup>21</sup> Inspired by the report of the SE of

[ $n$ ]circulenes,<sup>22</sup> we have successfully developed a method for calculating the SE of CNBs, where the strain-free total energy of a repeat unit of a CNB is calculated by a linear regression analysis.<sup>21</sup> This method can be considered as the homodesmotic reactions using a repeat unit of infinitely large CNBs as reference. However, the generality of this method has not been well investigated, and particularly, it is still unclear whether the method can be applied to CNBs comprising helicene structures. The investigation of a general and reliable SE analysis method is necessary for the development of the synthetic chemistry of CNB and related molecules.<sup>23</sup>

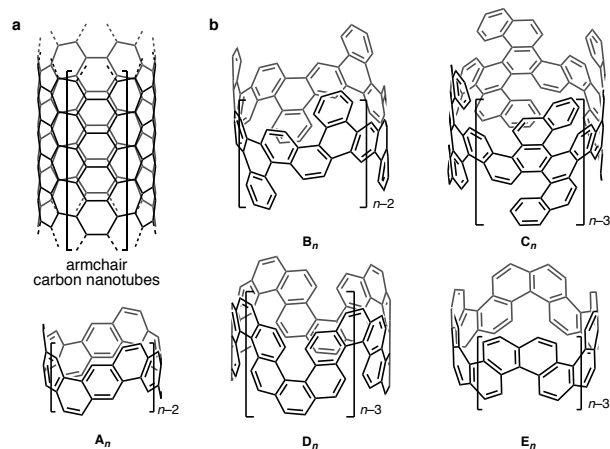


Fig. 1 (a) Structures of armchair CNTs and CNBs ( $A_n$ ) where  $n$  is the number of repeat unit. (b) CNBs containing [4]- or [5]helicene structures ( $B_n$ – $E_n$ ) where  $n$  is the number of repeat unit;  $B_n$  ( $n = 6$ ) is the simplified structure of synthesized (18,12)CNB<sup>9</sup> while  $C_n$ – $E_n$  are proposed in this work.

Herein, we report the SE calculation of helicene-containing CNBs. For this purpose, we proposed a hybrid method of conventional homodesmotic reactions and linear regressions. It was found that this method can be applied to CNBs containing helicene structures in their side chains as well as main chains.

First, the applicability of our linear regression method to helicene-containing CNBs was investigated. DFT calculation with B3LYP level of theory and 6-31G(d) basis sets were used.<sup>24–26</sup> Fig. 2 shows the plots of the total energy of CNBs  $A_n$  ( $n = 4$ –16) and  $B_n$  ( $n = 4$ –14) per number of repeat units as a function

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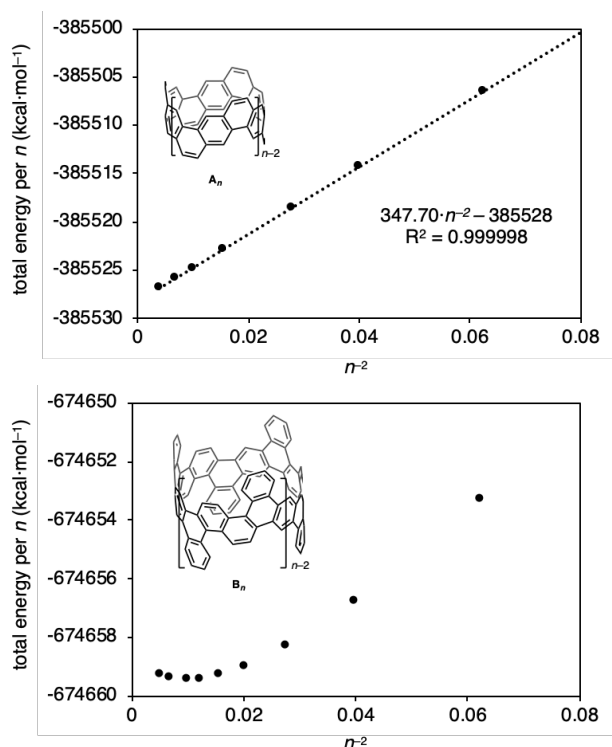
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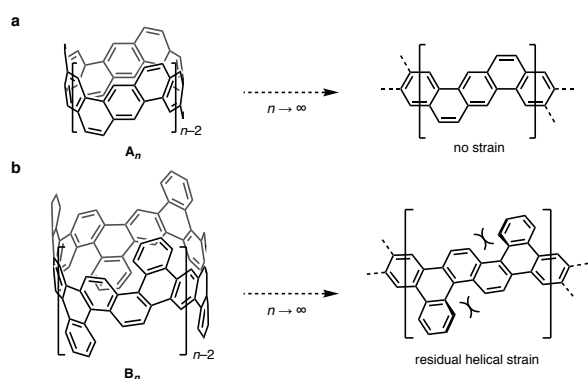
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Electronic Supplementary Information (ESI) available: Details of calculations and Cartesian coordinates of optimized structures. See DOI: 10.1039/x0xx00000x

of  $n^{-2}$ . Similar to the reported analysis ( $n = 3-6$ ),<sup>13</sup> the plots of  $A_n$  fit perfectly to a straight line (Fig. 2a) even in the larger sized region ( $n = 7-16$ ). In contrast, we found that the plot of  $B_n$  deviated from a straight line when the large-sized CNBs ( $n = 10-14$ ) were applied (Fig. 2b). This plot clearly indicated that our linear regression analysis could not be applied to  $B_n$ . The reason for this may be that the helical strain remained in  $B_n$  with an infinite size ( $n \rightarrow \infty$ , Fig. 3b), whereas  $A_n$  converged to a completely flat and strainless structure as the size increased (Fig. 3a). Thus, a modification of our method is required to cover a broad range of CNB structures, especially those comprising helicene substructures.



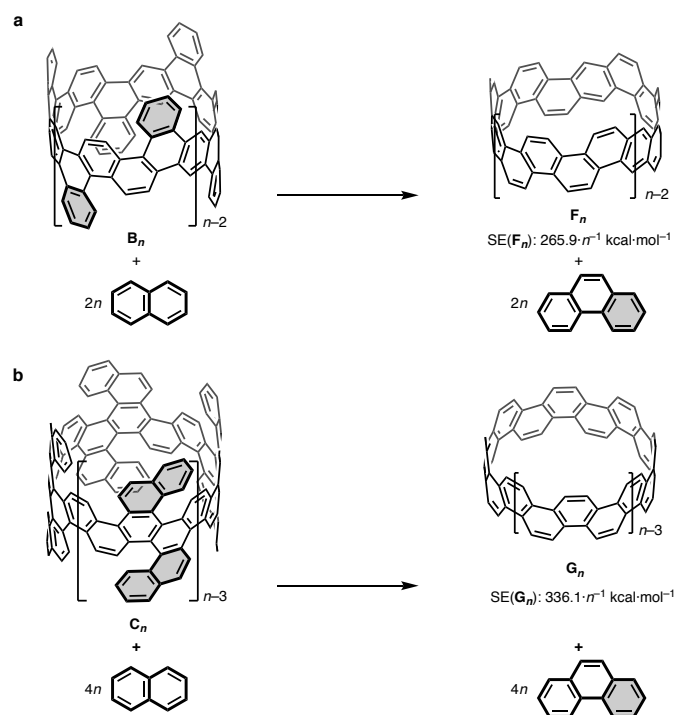
**Fig. 2** Total energy per number of repeat units ( $n$ ) of  $A_n$  (a) and  $B_n$  (b) as a function of  $n^2$  with a linear regression line.



**Fig. 3** (a) The structures of  $A_n$  with finite and infinite diameters. (b) The structures of  $B_n$  with finite and infinite diameters.

To address this issue, the linear regression analysis and conventional homodesmotic reaction were combined. In the first step, a homodesmotic reaction was applied to  $B_n$  to remove

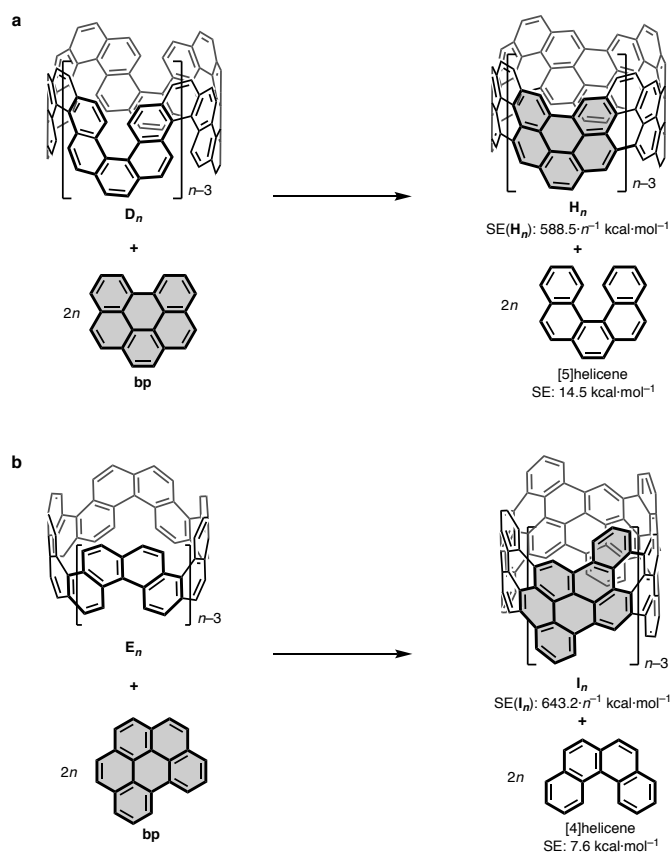
the benzene ring of each [4]helicene moiety (retro-benzannulation) and convert  $B_n$  into a non-helicene CNB  $F_n$  (Fig. 4a). The heat of formation of  $F_n$  was calculated by using naphthalene and phenanthrene as strainless reference molecules (See Scheme S2 in SI for details). In the second step, linear regression analysis was applied to  $F_n$  to determine its strain energies as a function of  $n$ . The  $SE(F_n)$  was determined to be  $265.9 \cdot n^{-1}$  kcal·mol<sup>-1</sup> with a high reliability (see Fig. S4 in SI for details). Finally the two values, that is, the heat of formation from  $B_n$  to  $F_n$  and the  $SE(F_n)$ , were combined to obtain the  $SE(B_n)$ . The obtained  $SE(B_n)$  values were 85.9 ( $n = 4$ ), 90.1 ( $n = 5$ ) and 99.1 ( $n = 6$ ) kcal·mol<sup>-1</sup> (See Table S2 in SI for other  $n$  values). Those values are similar to the  $SE$  values estimated solely by homodesmotic reactions (Scheme S1 in SI) reflecting the reliability of the current method. This hybrid method can also be applied to [5]helicene-containing CNBs. CNB  $G_n$  is the corresponding non-helicene structures for [5]helicene-containing CNB  $C_n$ . Hypothetically, the conversion from  $C_n$  to  $G_n$  can be carried out by using an appropriate amount of naphthalene and phenanthrene (double retro-benzannulation), as shown in Fig. 4b. The heat of formation ( $11-32$  kcal·mol<sup>-1</sup> for a repeat unit depending on  $n$ ) and the  $SE(G_n)$  values ( $336.1 \cdot n^{-1}$  kcal·mol<sup>-1</sup>) afforded the  $SE(C_n)$  ( $n = 3-8$  and 15, Table S3 in SI). The proposed method is simple and generally applicable to helicene-containing CNBs that can be converted into non-helicene CNBs by hypothetical retro-benzannulation reactions.



**Fig. 4** Schemes for determining the  $SE$  of  $B_n$  (a) and  $C_n$  (b). Homodesmotic reactions from helicene-containing CNBs ( $B_n$ ,  $C_n$ ) to non-helicene CNBs ( $F_n$ ,  $G_n$ ), and the  $SE$  of  $F_n$  and  $G_n$  as functions of  $n$  obtained by the linear regression method.

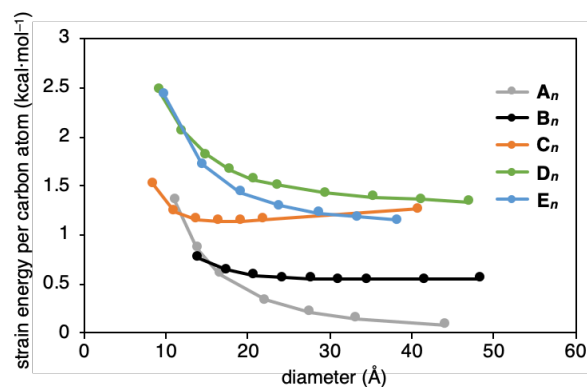
Subsequently, the CNBs with helicene structures in the main chain were studied. The CNBs  $D_n$  and  $E_n$  were designed as representatives for the category of helicene-containing CNBs

that could not be converted into non-helicene CNBs by hypothetical retro-benzannulation reactions. Alternatively, we found that the hypothetical C–C bond formation and benzannulation reactions are applicable for the conversion of CNBs such as  $D_n$  ( $n = 3-8, 10, 12, 14$  and  $16$ ) and  $E_n$  ( $n = 4, 6, 8, 10, 12, 14$  and  $16$ ) into the corresponding non-helicene CNBs  $H_n$  and  $I_n$ , respectively. As shown in Fig. 5a, the homodesmotic reaction of  $D_n$  was completed using benzo[ghi]perylene (**bp**, SE = 0), [5]helicene (SE = 14.5 kcal·mol<sup>-1</sup>; see Scheme S2 in SI)<sup>27,28</sup> and  $H_n$  (SE = 588.5  $n^{-1}$  kcal·mol<sup>-1</sup>; see Fig. S6 in SI). Similarly, SE( $E_n$ ) was successfully analyzed by using **bp**, [4]helicene (SE = 7.6 kcal·mol<sup>-1</sup>; see Scheme S2 in SI) and  $I_n$  (643.2  $n^{-1}$  kcal·mol<sup>-1</sup>; see Fig. S9 in SI) as shown in Fig. 5b. Since the term CNB has been defined as fully fused molecules representing the sidewall structure of CNTs, [6]- or higher helicene structures could not be included in this category because of the overlapping of carbon atoms in such higher helicenes. Thus, we conclude that our hybrid method compensates for the limitations of the previous method, and covers all the possible CNB structures.



**Fig. 5** Schemes for determining the SE of  $D_n$  (a) and  $E_n$  (b). Homodesmotic reactions from helicene-containing CNBs ( $D_n$ ,  $E_n$ ) to non-helicene CNBs ( $H_n$ ,  $I_n$ ), and the SE of  $H_n$  and  $I_n$  as the functions of  $n$  obtained by the linear regression method.

The thus-obtained SEs for  $A_n-E_n$  were summarized in Tables S2–S5, and Fig. 6 shows the plots of the SEs divided by the number of carbon atoms versus their diameters. While the SE of  $A_n$  converges to zero as the size increases, SE values remain in the case of  $B_n-E_n$  because of the contribution of helicene moieties.



**Fig. 6** Plot of the SE per carbon atom (kcal·mol<sup>-1</sup>) for  $A_n-E_n$  versus their diameters.

Finally, the change in the SE during the synthesis of chiral (18,12)CNB was analyzed to demonstrate the benefit of the current method in devising a synthetic strategy for CNBs. Compounds  $B_6$ ,  $J_6$ , and  $K_6$  shown in Fig. 7 correspond to (18,12)CNB, its starting material and the hypothetical intermediate before the last C–C bond formation step via the Scholl reactions,<sup>29,30</sup> respectively. While the previously reported SE values of  $B_6$  and  $J_6$  calculated by our linear regression method were 28.2 and 39.1 kcal·mol<sup>-1</sup>, respectively, we are skeptical regarding this "strain-decreasing" synthesis. The SE of  $J_6$  was determined to be 41.3 kcal·mol<sup>-1</sup> (Scheme S3 in SI) as calculated by the homodesmotic reaction according to the method for cycloparaphenylenes.<sup>20</sup> The suitable homodesmotic reactions including retro-benzannulation of [4]helicene moieties were applied to  $K_6$  to estimate its SE values as 95.9 kcal·mol<sup>-1</sup> (Scheme S3 in SI). As summarized in Fig. 7, the SEs gradually increased in the reaction sequence from  $J_6$  through  $K_6$  to  $B_6$ . The average increase in the strain with each C–C bond formation is 4.8 kcal·mol<sup>-1</sup> (12 C–C bonds from  $J_6$  to  $B_6$ ). Considering the increase in the SE for the last-bond formation (3.2 kcal·mol<sup>-1</sup> from  $K_6$  to  $B_6$ ), it may be stipulated that the successful C–C bond formation reactions from  $J_6$  to  $B_6$  is due to the gradual and relatively small strain increase for each step.

In conclusion, we have successfully estimated the strain energies of CNBs containing [4]- and [5]helicene moieties. Through the calculation of CNB  $B_n$ , we revealed that our previously reported method, linear regression analysis, is not applicable to helicene-containing CNBs. The newly developed method, combining the conventional homodesmotic reactions and linear regression analysis, was successful for the determination of the strain energies of CNBs  $B_n$  and  $C_n$  that have helicene moieties in their side chains. By changing the reference molecules for the homodesmotic reactions, the strain energies of CNBs with helicene structures in the main chains ( $D_n$  and  $E_n$ ) were also determined. The strain transition in the synthesis of (18,12)CNB was re-analyzed by the current method to confirm that the gradual and small increase in strain could be the key for the successful synthesis of the (18,12)CNB via Scholl reactions. Since general and reliable analytical methods are useful for predicting the properties and establishing synthetic routes for highly strained molecules, we believe this work will be an important step in the synthetic chemistry of CNBs.

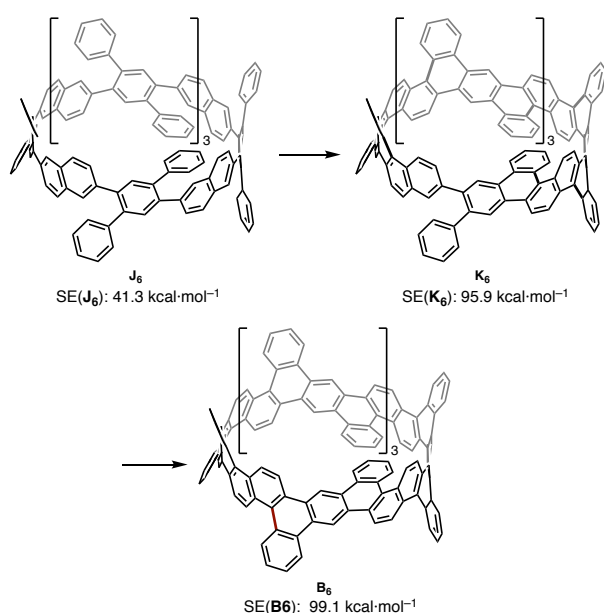


Fig. 7 Analysis of the strain increase from  $J_6$  to  $B_6$ .

This work was supported by the ERATO program from JST (JPMJER1302 to K.I.), the Funding Program for KAKENHI from MEXT (JP1905463 to K.I.; JP19H02701, and JP19K22183 to Y.S.), and The Murata Science Foundation (Y.S.). K.W. acknowledges Special Inter-University Researcher program in Institute for Molecular Science. The authors thank K. Y. Cheung and H. Shudo for fruitful comments. Calculations were performed using the resources of the Research Center for Computational Science, Okazaki, Japan. We would like to thank Editage (www.editage.com) for English language editing. ITbM is supported by the World Premier International Research Center Initiative (WPI), Japan.

## Conflicts of interest

There are no conflicts to declare.

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