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A Theoretical Study on the Strain Energy of Carbon Nanobelts

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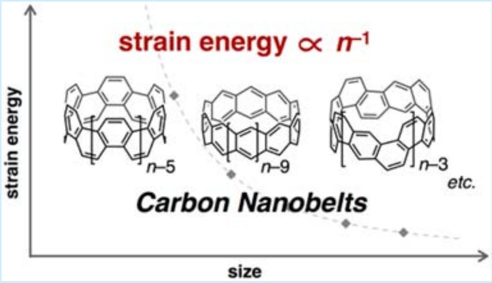
Supporting Information

ABSTRACT: A theoretical study on the strain energy of carbon nanobelts, i.e. the belt-shaped molecules representing the sidewall structures of carbon nanotubes, is reported. The strain energy of carbon nanobelts with chiral indices (*n*,*n*), (*n*,0), and (*n*,*m*) was determined without considering hypothetical homodesmotic reactions. The calculated difference between the strain energy of carbon nanobelts and their possible precursors is expected to be of great utility for future synthetic purposes.



Ring-shaped aromatic hydrocarbons that represent the sidewall segment of carbon nanotubes (CNTs, Figure 1a), the so-called "carbon nanorings (CNRs)", have received much attention on account of their radial π-conjugation, porous structure, and potential applications in CNT synthesis.[1] CNRs are obtained by "slicing" CNTs and are subdivided into three classes: armchair, zigzag, and chiral. Representative examples for these CNR classes are cycloparaphenylene (CPP),[1,2] cyclometaphenylene,[3] and cyclo-2,6-naphthylene,[4] respectively (Figure 1b). Although CPPs have been a synthetic target for organic chemists since the 1930s,[5] their high ring strain had prevented their synthesis until recently. In 2008, Bertozzi and Jasti reported the first synthesis of [9], [12], and [18]CPP using 1,4-cyclohexadienediyl units for the construction of unstrained macrocyclic precursors.[6] Since then, the groups of Jasti, Itami, and Yamago have synthesized CPPs of varied ring sizes using such unstrained precursors,[2] and the same synthetic strategies have also been applied in the synthesis of ring-shaped molecules including zigzag and chiral CNRs.[2,4,7,8]

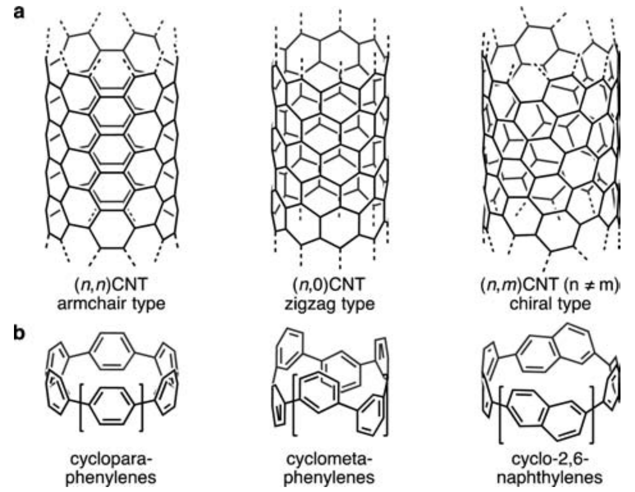


Figure 1. (a) Carbon nanotubes (CNTs) and (b) carbon nanorings (CNRs).

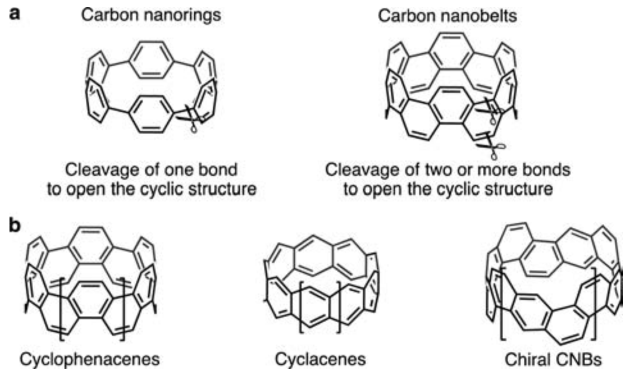


Figure 2. (a) Definitions of CNRs (left) and CNBs (right) used in this study. (b) Representative examples for CNBs.

The next challenging targets in this research field are the so-called carbon nanobelts (CNBs), which have not yet been synthesized. Our definition and the characteristics of CNRs and CNBs are as follows: (i) CNRs and CNBs are the hydrocarbon molecules that represent the sidewall segments of CNTs; (ii) upon cleavage of one C−C bond, CNRs open to give a linear structure (Figure 2a, left), while, for CNBs, cleavage of at least two C−C bonds is necessary in order to open their cyclic structures (Figure 2a, right). Cyclophenacenes, cyclacenes, and chiral CNBs represent typical examples of armchair, chiral, and

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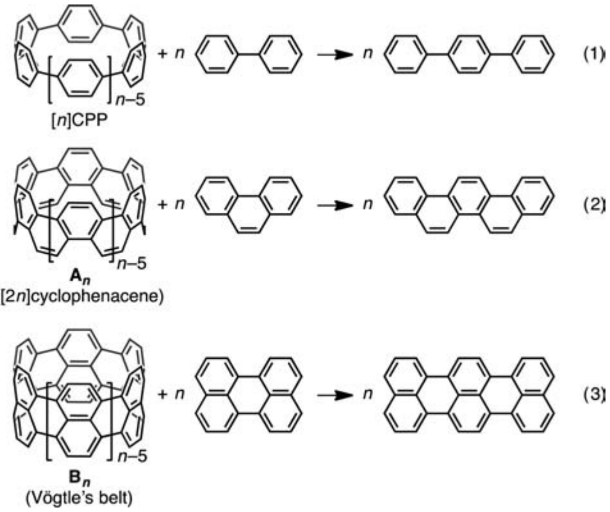
zigzag CNBs, respectively (Figure 2b). Despite the considerable synthetic efforts,[9] CNBs have not yet been synthesized successfully. Nakamura and co-workers have, however, synthesized a multisubstituted fullerene C_{60}, which exhibits the π-conjugated substructure of a cyclophenacene.[10]

In an attempt to quantify this synthetic challenge, we herein report theoretical calculations on the determination of the strain energy (SE) of CNBs using the Gaussian 09 program[11a] with the B3LYP/6-31G(d) level of theory.[11b,c] Although theoretical studies on the structure, aromaticity, molecular orbitals, energy gaps, and reactivity of CNBs have already been performed,[12] reports on a systematic study of their SEs still remain elusive.[12h] The SE of highly strained molecules has a significant impact on their stability and reactivity, which thus determines their synthetic accesibility.[13] The quantitative analysis of the SE of CNBs accordingly represents a desirable research target in order to prepare synthetic studies.

Initially, we tried to calculate the intrinsic SE of CNBs via hypothetical homodesmotic reactions,[14] the standard method.[15,16] Previously, we have calculated the SE of [n]CPPs as the reaction heat (ΔH/kcal mol^{-1}) of the homodesmotic reaction shown in eq 1.[17] The SE of [n]CPPs is thereby inversely proportional to n (Figure 3, solid line), which indicates that the limit of the SE for [∞]CPP is 0 kcal mol^{-1}. However, we found that the same method could not be applied to CNBs. The corresponding hypothetical reactions for the calculation of the SE of cyclophenacenes (**A**$_n$) and Vögtle's belts[18] (**B**$_n$) are shown in eqs 2 and 3. Based on these equations, the reaction heat was plotted as a function of n^{-1} (Figure 3). In contrast to [n]CPPs, the SE did not converge to zero but to negative values, i.e. −8.3 and −36.5 kcal mol^{-1} for **A**$_n$ and **B**$_n$, respectively. We also tried different hypothetical reactions and other CNBs including zigzag and chiral ones, but a reasonable result could not be obtained for any of the examined combinations (for details, see the Supporting Information). This indicates that the hypothetical reactions for CNBs should not be homodesmotic, probably due to the difference in bond order between the cleaved and the newly formed C−C bonds. We therefore concluded that it should be very difficult to find a suitable homodesmotic reaction for each CNB type.



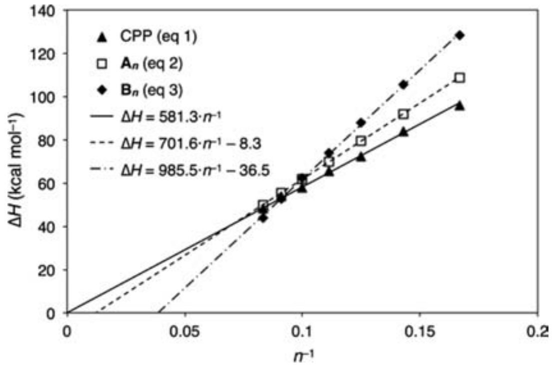


Figure 3. Reaction heat (ΔH) for [n]CPPs, **A**$_n$, and **B**$_n$ (n = 6−12) as a function of n^{-1} with linear regression lines.

Subsequently, we attempted a different method for the estimation of the SE of CNBs. Hopf and co-workers used a method to calculate the SE of [n]circulenes that did not rely on hypothetical reactions.[19] They simply compared the total energy of a repeat unit (C_4H_2) with the value of [6]circulene (coronene), which is the only unstrained circulene. We anticipated that a similar method should also be applicable to symmetric molecules such as CNBs. In the case of CNBs, CNB with an infinite ring size (n = ∞) can be regarded as unstrained. Figure 4a and 4b show the total energy of a repeat unit (C_8H_4) for **A**$_n$ (E(**A**$_n$)·n^{-1}) as a function of n and n^{-1}, respectively, and the plot in Figure 4b fits the following equation perfectly (R^2 > 0.99999):

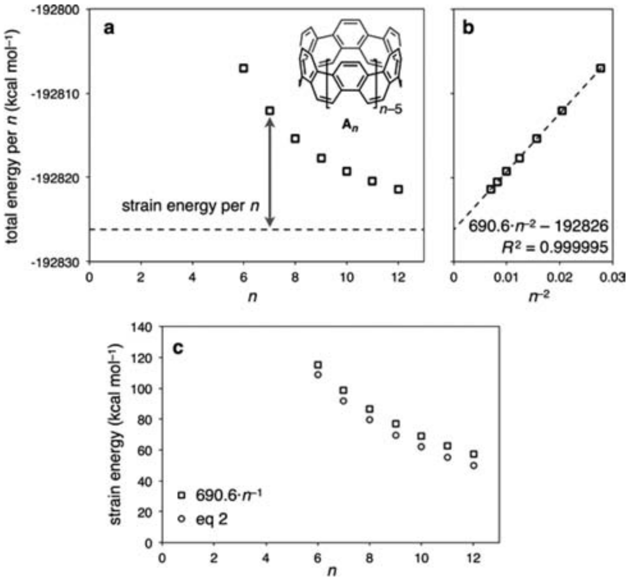


Figure 4. Total energy per number of repeat units (n) of **A**$_n$ as a function of n (a) and n^{-2} with a linear regression line (b). SEs of **A**$_n$ obtained by the current method (□) and by eq 2 (○) (c).

$$E(\mathbf{A}_n)\cdot n^{-1} = 690.6\cdot n^{-2} - 192826\ \text{kcal mol}^{-1}$$

This equation indicates that the limit of E(**A**$_n$)·n^{-1} for n = ∞ is −192826 kcal mol^{-1}, and that 690.6·n^{-2} kcal mol^{-1} should therefore be considered as the SE of the repeat unit in **A**$_n$. Thus, the SE can be determined as 690.6·n^{-1} kcal mol^{-1}. SEs of **A**$_n$ obtained by eq 2 and the current method are summarized in Figure 4c.

We further found that this method is generally applicable for a wide variety of symmetric CNBs. The SEs of CNBs as a function of n are summarized in Figure 5a. In addition to those

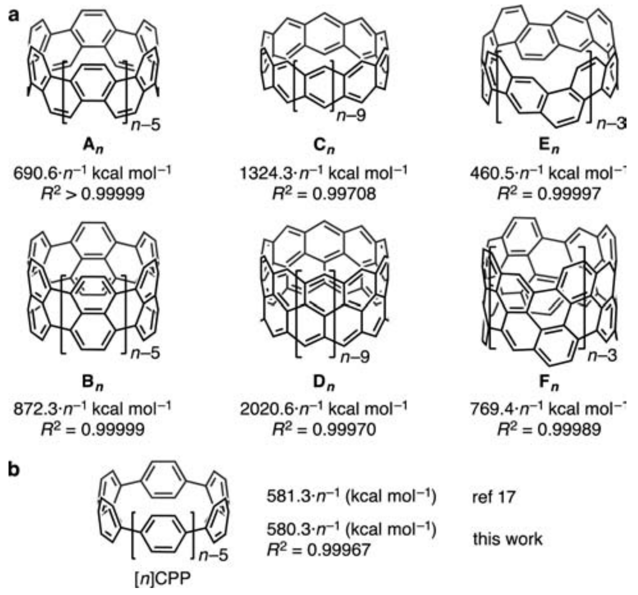


Figure 5. SE for CNBs (a) and CPPs (b) as a function of n^{-1}.

for armchair CNBs ($\mathbf{A}_n$, $\mathbf{B}_n$), the SE of zigzag ($\mathbf{C}_n$, $\mathbf{D}_n$) and symmetric chiral CNBs ($\mathbf{E}_n$, $\mathbf{F}_n$), which represent the sidewall segment of ($2n$,n)CNTs, could also be obtained successfully. According to Houk's report on the [n]cyclacenes ($\mathbf{C}_n$) and zigzag CNBs ($\mathbf{D}_n$),[20] the energies of open-shell singlet states of $\mathbf{C}_n$ and $\mathbf{D}_n$ were used to obtain SEs.[21] It is worth noting that the current method was able to accurately reproduce the SEs of [n]CPPs obtained from the homodesmotic reaction (Figure 5b),[17] which demonstrates the high reliability of the new method.

In order to assess the general applicability of this method, we calculated the SE of an unsymmetric CNB, i.e. a chiral (7,6)CNB ($\mathbf{G}_1$ in Figure 6). For that purpose, we initially expanded the structure of the (7,6)CNB to the corresponding (14,12), (21,18), and (28,24)CNBs ($\mathbf{G}_{2-4}$ in Figure 6). From the plot of the total energy of $\mathbf{G}_n$ per repeat unit ($E(\mathbf{G}_n)\cdot n^{-1}$) as a function of n^{-2}, the following equation was obtained:

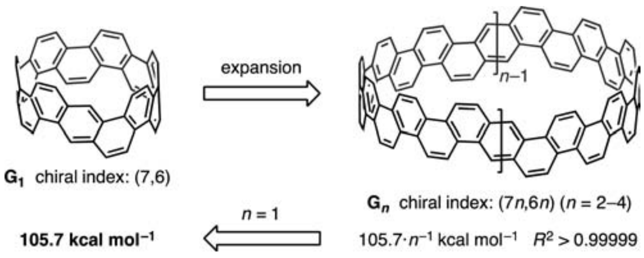
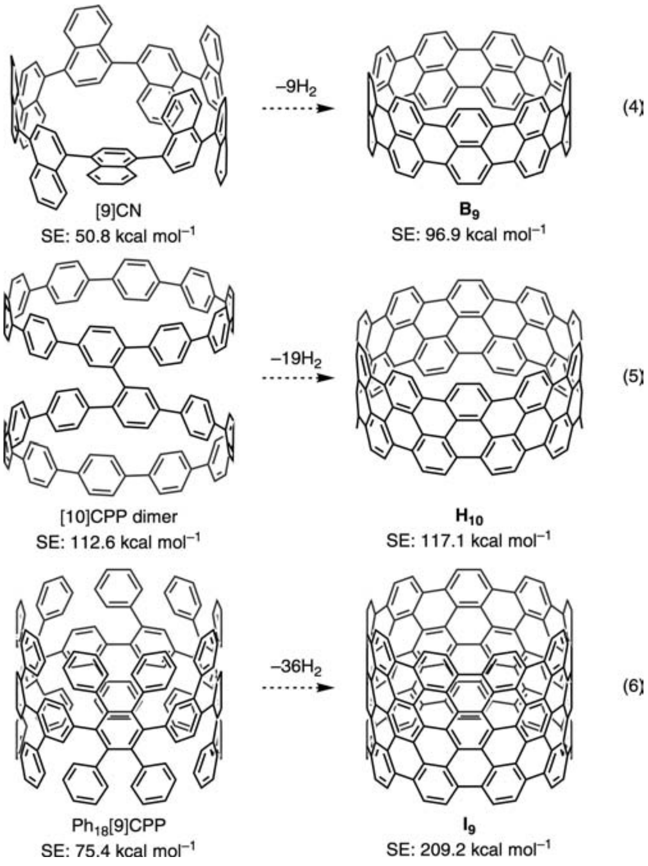


Figure 6. Method to calculate the SE of the (7,6)CNB ($\mathbf{G}_1$).

$$E(\mathbf{G}_n)\cdot n^{-1} = 105.7\cdot n^{-2} - 1253369\ (\text{kcal mol}^{-1})$$

Thus, the SE of $\mathbf{G}_1$ is 105.7 kcal mol^{-1}, which shows that this strategy is applicable to any chiral (n,m)CNBs, even in the absence of symmetry, i.e. when n and m do not share a common divisor.

With the SE of CNBs in hand, we were able to estimate the synthetic challenge of making them. The three CNRs, [9]cyclonaphthylene ([9]CN),[8c] [10]CPP dimer,[8i] and Ph$_{18}$[9]CPP,[8j] are the molecules that could potentially be converted into their corresponding CNBs ($\mathbf{B}_9$, $\mathbf{H}_{10}$, and $\mathbf{I}_9$, respectively) by multiple dehydrogenative cyclization reactions (eqs 4−6). The SEs of [10]CPP dimer, Ph$_{18}$[9]CPP, $\mathbf{H}_n$, and $\mathbf{I}_n$ were determined to be 112.6, 75.4, 1171·n^{-1}, and 1883·n^{-1} kcal mol^{-1}, respectively (see the Supporting Information for details). The conversion of the [10]CPP dimer into $\mathbf{H}_{10}$ induces only a minor amount of additional strain (4.5 kcal mol^{-1}), while the other two reactions involve a significant increase in strain (46.1 and 133.8 kcal mol^{-1} for [9]CN and Ph$_{18}$[9]CPP, respectively). These results thus represent the first quantification of the energetic requirements for the synthesis of CNBs on the basis of their intrinsic SEs.



In summary, we have successfully established a general method for the determination of the SE of CNBs. The linear regression analysis of the total energy of CNBs per repeat unit as a function of n^{-2} afforded the SEs of CNBs as a function of n^{-1}. This method is applicable not only to symmetric CNBs with (n,n), (n,0), and ($2n$,n) chiral indices but also to unsymmetric (n,m)CNBs where n and m do not share a common divisor. The present method should thus facilitate the design of realistic synthetic pathways to CNBs, based on the comparison between the SE values of CNBs and those of their potential precursors.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b00365.

Calculation details (PDF)
Cartesian coordinates of optimized structures (ZIP)

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Notes

The authors declare no competing financial interest.

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