Strain Visualization for Strained Macrocycles

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1. General Experimental Details

All glassware was flame dried and cooled under an inert atmosphere of nitrogen unless otherwise noted. Moisture sensitive reactions were carried out under nitrogen atmosphere using Schlenk and standard syringe/septa techniques. Dichloromethane was dried by filtration through alumina according to the methods describes by Grubbs.¹ ¹H NMR spectra were recorded at 500 MHz on a Bruker Advance-III-HD NMR spectrometer. ¹³C NMR spectra were recorded at 125 MHz on a Bruker Advance-III-HD NMR spectrometer. All ¹H NMR spectra were taken in chloroform- d (referenced to TMS, δ 0.00 ppm). All ¹³C NMR spectra were taken in chloroform-d (referenced to chloroform, δ 77.16 ppm). All reagents were obtained commercially unless otherwise noted. Mass spectra were obtained from the University of Illinois at Urbana-Champaign Mass Spectrometry Lab using ESI on a Micromass 70-VSE.

1. Freshly synthesized m[6]CPP² (8 mg, 17.5 nmol, 1 equiv) was added to a flame dried 25 mL round bottom flask. The contents were evacuated and backfilled with nitrogen three times. Dichloromethane (6 mL) was added to the flask. This was cooled to -20 °C. A 50 mM solution of Br₂ (64.0 µL) in methylene chloride (50 mL) was prepared in a flame dried 100 mL pear shaped shaped flask. The bromine solution (385 µL, 19.3 nmol, 1.1 equiv) was added dropwise and the mixture was stirred at -20 °C for 20 min. The contents of the flask were passed through an Aura MT 0.45 µm PTFE syringe filter and evaporated under reduced pressure to obtain 1 as an orange-red solid (8.7 mg, 81%). ¹H NMR (500 MHz, Chloroform-d) δ 7.49 – 7.40 (m, 3H), 7.36 (d, J = 8.5 Hz, 4H), 7.33 (d, J = 8.4 Hz, 4H), 7.18 (d, J = 8.5 Hz, 4H), 7.11 (d, J = 8.4 Hz, 4H), 6.38 (s, 4H), 4.65 (t, J = 1.7 Hz, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 143.35, 142.82, 142.69, 141.66, 140.34, 139.15, 130.35, 130.27, 129.08, 127.32, 126.78, 121.81, 56.44, 1.17. HRMS (ESI-TOF) (m/z): [M-HBr]⁺ calculated for C₉₆H₇₃Br, 534.09831; found, 534.09804.
2. Comments on Calculations

Throughout the development of this program when fragments were clearly able to relax into perfectly flat aromatic hydrocarbons (fragments of CPPs or cyclophenacenes) the program worked best. This appears to be due to a clear and obvious trajectory on a potential energy surface between the strained and unstrained states and a finite end with a single conformation. When the trajectory is not so clear, as in the case of fragments with little strain (~10 kcal/mol or less) or alkyl chains (cyclophanes), more oversight by the user is required to acquire accurate results. There are two optimization errors that often lead to poor quality results. Non-converging optimizations where small changes in energy add up over many non-convergent cycles and instances where the algorithm takes a step into a high energy state. The program alerts the user if problems like this occur. This led to the use of the quasi-Newton rational function optimization algorithm for optimization, however, using this algorithm does not always solve these issues. When necessary, calculating frequencies at each step does solve this problem in every instance tested, however, at a higher computational expense.

3. Fragments used for strain calculations

All details for running calculations can be found at https://github.com/CurtisColwell/StrainViz

All input files, fragment geometries, and output files are available for download. Fragment geometries are shown below and in .xyz format.

Fragments used for Figure 4

Fragment size 2

|   |   |   |   |
|---|---|---|---|
| 1 | 2 | 3 | 4 |
| 5 | 6 | 7 | 8 |
Fragment size 3

1  2  3  4

5  6  7  8

Fragment size 4

1  2  3  4

5  6  7  8
Fragment size 5

|   |   |   |   |
|---|---|---|---|
| 1 | 2 | 3 | 4 |
| 5 | 6 | 7 | 8 |

Fragment size 6

|   |   |   |   |
|---|---|---|---|
| 1 | 2 | 3 | 4 |
| 5 | 6 | 7 | 8 |
Fragment size 7

|   |   |   |   |
|---|---|---|---|
| 1 | 2 | 3 | 4 |
| 5 | 6 | 7 | 8 |

Fragments used for Figure 5

[10]CPP

|   |   |   |   |
|---|---|---|---|
| 1 | 2 | 3 | 4 |
| 5 | 6 | 7 | 8 |
[9] CPP
[6]CPP

[6]cyclophenacene
[2.2]paracyclophane

[2](6,1)Naphthaleno[1]Paracyclophane

Fragments used for Figure 6

m[6]CPP
Fragments used for Figure 7

dibromo[6]CPP

| 1 | 2 | 3 | 4 |
|---|---|---|---|

| 1 | 2 |
|---|---|

Fragments used for Figure 8

Tanaka Belt

| 1 | 2 | 3 | 4 |
|---|---|---|---|
Möbius Tanaka Belt

| 1 | 2 | 3 |
|---|---|---|
| 4 | 5 |   |

Vögtle Belt

| 1 | 2 | 3 | 4 |
|---|---|---|---|
| 5 | 6 | 7 | 8 |
Vögtle Möbius

Fragments used for Figure 9

Ball

Panel
Fragments used for Figure 10

**Cyclooctyne**

1. 
2. 
3. 
4. 

**trans-cyclooctene**

1. 
2. 
3. 
4. 

**trans-bicyclo[6.1.0]nonene**

1. 
2. 
3. 
4. 

4. References

(1) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. Safe and Convenient Procedure for Solvent Purification. *Organometallics* **1996**, *15*, 1518–1520.

(2) Lovell, T. C.; Colwell, C. E.; Zakharov, L. N.; Jasti, R. Symmetry Breaking and the Turn-on Fluorescence of Small, Highly Strained Carbon Nanohoops. *Chem. Sci.* **2019**, *10*, 3786–3790.