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# Conformational analysis of bridgehead-substituted bicyclo[*m*.*m*.*m*]alkanes and bicyclo[8.8.*n*]alkanes

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ABSTRACT

Conformational analyses of bicyclo[*m*.*m*.*m*]alkanes where $m$=1–10 and of bicyclo[8.8.*n*]alkanes where $n$=1–7 bearing methyl groups on the bridgeheads were carried out using a Monte Carlo search strategy. In the bicyclo[*m*.*m*.*m*]alkane series, greater variability was observed for the inter-bridgehead distance for larger values of $m$. This suggests that properly substituted bicyclo[8.8.8]hexacosanes or larger ring systems might serve as molecular springs.

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## 1. Introduction

Small bicycles, such as 1,3-dimethylbicyclo[1.1.1]pentane (**1**)[1] and 1,4-dimethylbicyclo[2.2.2]octane (**2**),[2] possess little conformational freedom, and so the methyl substituents attached to the bridgehead atoms are directed outward, away from the bicyclic core. Larger bicycles with sufficiently long bridges may exist as configurationally diastereomeric *in*,*in*/*out*,*out* and *in*,*out*/*out*,*in* conformer pairs.[3] For example, only *in*,*out*-bicyclo[4.4.4]tetradecane (**3**) is known,[4] while *in*,*in*-bicyclo[8.8.8]hexacosane (**4a**) and *in*,*out*-bicyclo[8.8.8]hexacosane (**4b**) are both known.[5]

Large bicycles can adopt multiple conformations. Saunders examined the conformations and energies of 32 aliphatic bicycles using Monte Carlo conformational search techniques.[6] Among other observations, he predicted that the *in*,*out*, *out*,*out*, and *in*,*in* forms of bicyclo[6.5.1]tetradecane (**5a**–**c**) would have comparable strain energies (168.1, 176.4, and 177.6 kJ/mol, respectively). In proof of this prediction, all three isomers were subsequently prepared and characterized.[7]

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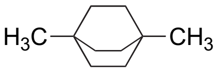

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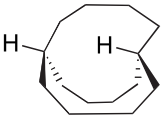

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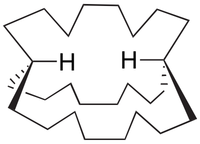

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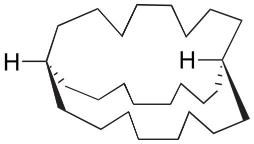

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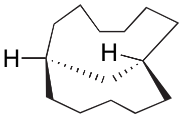

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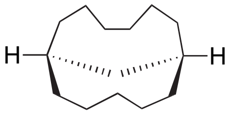

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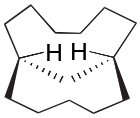

**5c**

We previously prepared *out*,*out*-1,10-dimethylbicyclo[8.8.8]-hexacosane (**6**) and *out*,*out*-1,10-dihydroxybicyclo[8.8.8]hexacosane (**7**).[8] Crystallographic analysis of **7** revealed 'spring-like'

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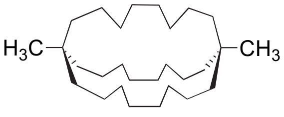
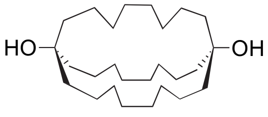
deformability in that the bridgehead-to-bridgehead distance ($\kappa$) varied among the four conformers present in the crystal by as much as 15%. One possible use for such 'molecular springs' might be to imbue otherwise rigid structures, for example, Kevlar®, with a measure of elasticity. To study the limits of this type of deformability, hereafter termed 'conformational compressibility', we carried out conformational analyses[9] of bicyclo[*m.m.m*]alkanes **1**, **2**, **6**, and **8**–**14** and also of bicyclo[8.8.*n*]alkanes **15**–**21** that bear methyl groups at the bridgeheads. Our findings are reported herein.



**6**



**7**

## 2. Results

Table 1 summarizes the results of the Monte Carlo searches for the populated conformers of bicyclo[*m.m.m*]alkanes **1**, **2**, and **6**–**14**. This search for 1,10-dimethylbicyclo[8.8.8]hexacosane (**6**) is represented graphically in Figure 1. Similar graphic summaries of the conformational searches for the other bicyclo[*m.m.m*]alkanes are given in Supplementary data that accompanies this article. Depicted in Figure 2 are the global minimum energy conformers (GMs) observed for each bicycle studied. Table 2 lists the energy, the number of times found, and the percentage of the population that each GM represents (at 300 K). In all cases, the global minimum was found repeatedly. Structural parameters descriptive of conformational compressibility along the inter-bridgehead axis and the relative orientations of the two bridgehead methyl groups are also given in Tables 1 and 2 and are defined and discussed below.

As expected, there are generally more low-energy conformers for bicycles of larger size. For example, two or fewer conformers were observed within 50 kJ of the GMs for compounds **1**, **2**, and **8**, while 34, 171, 677, and 6040 conformers were observed within this energy window for compounds **9**–**12**, respectively. All of the conformations observed within 50 kJ of the GMs for compounds **1**, **2**, **6**, **8**–**12**, and **14** possess *out*,*out* methyl orientations.[10] Apparently, insufficient room exists in the interior of these bicycles to accommodate a methyl group. In the case of 1,11-dimethylbicyclo[9.9.9]nonacosane (**13**), 14 conformers of the *in*,*out* configurational diastereomer were observed in addition to over 26,000 conformers of the *out*,*out* configurational diastereomer (see Table 1 and Fig. 2). No *in*,*in* structures were observed within 50 kJ of the *out*,*out* GM for any of the bicycles studied.

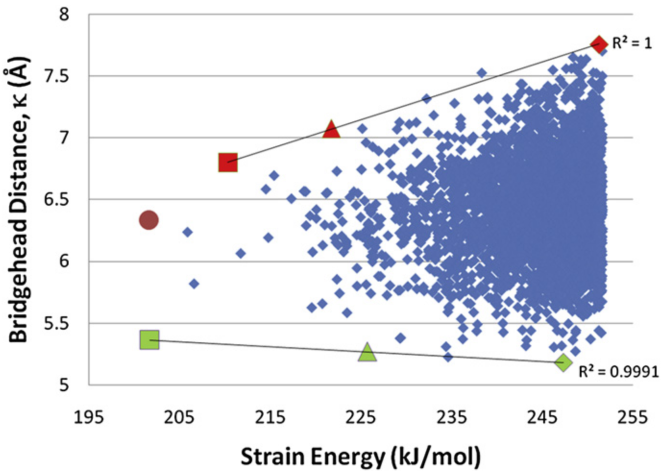


**Figure 1.** Distribution of conformers (◆) with respect to $\kappa$ and strain energy at 300 K for 1,10-dimethylbicyclo[8.8.8]hexacosane (**6**). ●=global minimum energy structure (GM); green ■, ▲, ◆=$\kappa_{min}$ within 10, 25, and 50 kJ of GM; ■, ▲, ◆=$\kappa_{max}$ within 10, 25, and 50 kJ of GM.

The strain energies observed for the GMs reflect the strain associated with the primary ring (Table 2).[11] Thus, compound **2** containing a six-membered primary ring is the least strained, compound **9** containing a 10-membered primary ring is the most strained, and bicycles containing primary rings progressively smaller or larger than 10-membered become progressively less strained. The bridgehead-to-bridgehead distance ($\kappa$) increases as the bicycles become larger. These trends are reflected in the weighted average strain energies and the population-weighted average inter-bridgehead distances ($\kappa_{ave}$) for this homologous series (see Supplementary data).

Values for $\Delta\kappa$, defined as $\kappa_{max}-\kappa_{min}$ observed within a given energy window, generally increase as the bicyclic system becomes larger (Table 2). Values for $\Delta\kappa$ also become larger for each bicyclic system as the energy window is expanded, e.g., from 10, to 25, to 50 kJ/mol above the energy of the GM. Thus, values of $\Delta\kappa$ reflect energy-dependent conformational compressibility along the axis connecting the bridgeheads. A plot of $\Delta\kappa$ and the percent conformational compressibility, defined as $100(\Delta\kappa/\kappa_{ave})$, versus bridge length ($m$) for bicyclo[*m.m.m*]alkanes **6** and **9**–**14** for the energy window 50 kJ/mol above the relevant GMs is depicted in Figure 3. It is evident that larger bicycles have significantly greater conformational compressibility along the inter-bridgehead axis.

**Table 1**
Monte Carlo search results for conformers of bicyclo[*m.m.m*]alkanes **1**, **2**, and **6**–**14**

| Compound | Name | Number of conformers[a] | $\Delta\kappa$[b] (Å) | $\kappa_{ave}$[c] (Å) | % Conformational compressibility[d] |
|---|---|---|---|---|---|
| **1** | 1,3-Dimethylbicyclo[1.1.1]pentane | 2 | 0 | 1.98 | 0 |
| **2** | 1,4-Dimethylbicyclo[2.2.2]octane | 1 | na | 2.63 | na |
| **8** | 1,5-Dimethylbicyclo[3.3.3]undecane | 2 | 0.05 | 3.42 | 0 |
| **9** | 1,6-Dimethylbicyclo[4.4.4]tetradecane | 34 | 0.76 | 4.45 | 17 |
| **10** | 1,7-Dimethylbicyclo[5.5.5]heptadecane | 171 | 0.98 | 4.89 | 20 |
| **11** | 1,8-Dimethylbicyclo[6.6.6]eicosane | 677 | 1.44 | 5.37 | 27 |
| **12** | 1,9-Dimethylbicyclo[7.7.7]tricosane | 6040 | 2.37 | 5.77 | 41 |
| **6** | 1,10-Dimethylbicyclo[8.8.8]hexacosane | 4242 | 2.68 | 5.90 | 44 |
| **7** | 1,10-Dihydroxybicyclo[8.8.8]hexacosane | 31,871 | 2.82 | 5.96 | 47 |
| **13** | 1,11-Dimethylbicyclo[9.9.9]nonacosane[e] | 26,038 | 3.58 | 6.78 | 53 |
| **14** | 1,12-Dimethylbicyclo[10.10.10]dotriacontane | 33,541 | 4.20 | 7.38 | 56 |

[a] Found within 50 kJ of the GM at 300 K.

[b] $\Delta\kappa=\kappa_{max}-\kappa_{min}$.

[c] $\kappa_{ave}=\sum$(population-weighted $\kappa$).

[d] % Conformational compressibility=$100(\Delta\kappa/\kappa_{ave})$.

[e] Fourteen conformers of the *in*,*out* configurational diastereomer were found within 50 kJ of the global minimum. They are not represented in the table. All other conformers found were of the *out*,*out* configurational diastereomer.

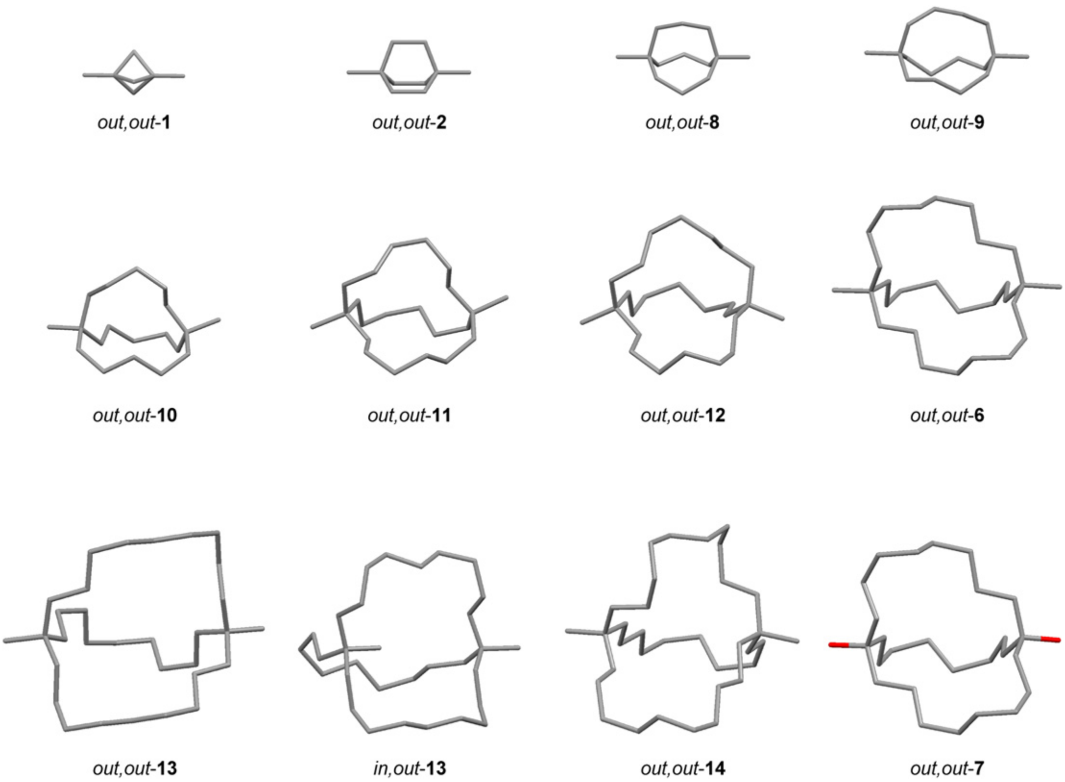


**Figure 2.** Global minimum energy structures (GMs) for bicycles **1**, **2**, and **6**–**14**. Also depicted is *in,out*-**13**, the lowest energy conformer (GM) of the *in,out* configurational diastereomer of 1,11-dimethylbicyclo[9.9.9]nonacosane. This structure is 24.2 kJ/mol higher in energy than the GM, *out,out*-**13**. Hydrogen atoms have been removed for clarity.

**Table 2**
Global minimum energy conformers of bicyclo[*m*.*m*.*m*]alkanes **1**, **2**, and **6**–**14**

| Compound | Name | Strain energy (kJ/mol) | Times GM found | % pop[a] | $\kappa$[b](Å) | $\gamma_1$[c] (°) | $\gamma_2$[c] (°) |
|---|---|---|---|---|---|---|---|
| **1** | 1,3-Dimethylbicyclo[1.1.1]pentane | 173 | 9744 | 100 | 1.97 | 180 | 180 |
| **2** | 1,4-Dimethylbicyclo[2.2.2]octane | 134 | 20,000 | 100 | 2.63 | 180 | 180 |
| **8** | 1,5-Dimethylbicyclo[3.3.3]undecane | 276 | 415 | 100 | 3.43 | 180 | 180 |
| **9** | 1,6-Dimethylbicyclo[4.4.4]tetradecane | 466 | 5 | 70 | 4.49 | 180 | 180 |
| **10** | 1,7-Dimethylbicyclo[5.5.5]heptadecane | 406 | 154 | 68 | 4.74 | 153 | 158 |
| **11** | 1,8-Dimethylbicyclo[6.6.6]eicosane | 309 | 42 | 26 | 5.35 | 156 | 155 |
| **12** | 1,9-Dimethylbicyclo[7.7.7]tricosane | 253 | 8 | 42 | 5.54 | 155 | 155 |
| **6** | 1,10-Dimethylbicyclo[8.8.8]hexacosane | 202 | 102 | 42 | 6.34 | 170 | 170 |
| **7** | 1,10-Dihydroxybicyclo[8.8.8]hexacosane | 184 | 9 | 16 | 6.12 | 168 | 168 |
| **13** | 1,11-Dimethylbicyclo[9.9.9]nonacosane | 200 | 2 | 34 | 7.12 | 160 | 160 |
| **14** | 1,12-Dimethylbicyclo[10.10.10]dotriacontane | 188 | 3 | 13 | 6.35 | 156 | 156 |

[a] The percent of the conformer population represented by the GM at 300 K.
[b] $\kappa$ is the distance between the bridgehead carbon atoms.
[c] $\gamma$ is the angle formed by the two bridgehead carbon atoms and one methyl carbon atom (or one hydroxyl oxygen atom in the case of **7**).

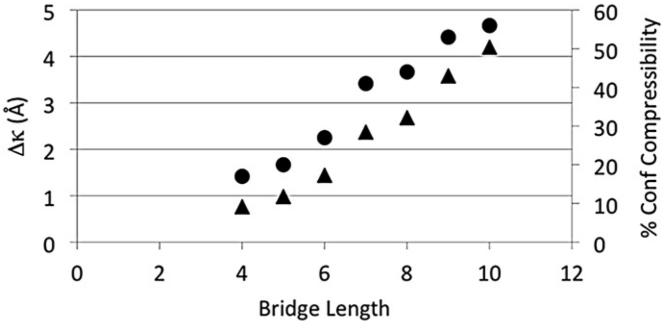


**Figure 3.** Plot of $\Delta\kappa$ (▲) and percent conformational compressibility (●) versus bridge length ($m$) for conformer populations within 50 kJ/mol of the GMs for bicyclo[*m*.*m*.*m*]alkanes **6** and **9**–**14**.

In the small *out*,*out* bicycles **1**, **2**, **8**, and **9**, the vectors that connect the bridgehead and attached methyl carbons are strictly collinear (see Table 2, $\gamma_1=\gamma_2=180°$) and are opposed. While there is some deviation from strict collinearity in the larger *out*,*out* bicycles **6** and **10**–**14**, the $\gamma$ values are all greater than 150°, and so the methyl substituents of *out*,*out* conformers can also be regarded as 'opposed'.

A similar conformational analysis was carried out for 1,10-dihydroxybicyclo[8.8.8]hexacosane (**7**). The GM, shown in Figure 2, is clearly related to the GM for **6**.[12] It is noteworthy that the four conformers observed in the crystal structure of **7** included the GM and three other conformers also observed in the ensemble generated by the conformational search.[8] Despite the smaller size of hydroxyl versus methyl groups[13] and the potential for intramolecular hydrogen bonding, no *in*,*in* or *in*,*out* structures were observed for **7** within 50 kJ of the GM. A much larger number of conformers was obtained for **7** than for **6** owing to the possible differences in the relative orientations of the hydroxyl groups.

Conformational analyses were also carried out for 1,10-dimethylbicyclo[8.8.$n$]alkanes **15**–**21** where $n$=1–7. Table 3 gives the results of these Monte Carlo searches, which are summarized graphically in the Supplementary data that accompanies this article. Figure 4 depicts the global minimum energy conformers (GMs) observed for each bicycle studied, and Table 4 lists the energy, the number of times found, and the percentage of the population that each GM represents. In all cases, the GM was found repeatedly. Structural parameters descriptive of the conformational compressibility along the inter-bridgehead axis and the relative orientations of the bridgehead methyl groups are also given in Tables 3 and 4 and are discussed below.

**Table 3**
Monte Carlo search results for conformers of bicyclo[8.8.$n$]alkanes **15**–**21** and **6**

| Compound | Name | Number of conformers[a] | $\Delta\kappa$[b] (Å) | $\kappa_{ave}$[c] (Å) | % Conformational compressibility[d] | $\gamma_{ave}$[e] (°) |
|---|---|---|---|---|---|---|
| **15** | 1,10-Dimethylbicyclo[8.8.1]nonadecane | 16 | 0.04 | 2.84 | 1 | 132 |
| **16** | 1,10-Dimethylbicyclo[8.8.2]eicosane | 45 | 0.09 | 4.04 | 2 | 114 |
| **17** | 1,10-Dimethylbicyclo[8.8.3]heneicosane | 58 | 0.68 | 5.17 | 13 | 139 |
| **18** | 1,10-Dimethylbicyclo[8.8.4]docosane | 70 | 0.73 | 5.23 | 14 | 171 |
| **19** | 1,10-Dimethylbicyclo[8.8.5]tricosane | 20 | 0.73 | 5.94 | 12 | 143 |
| **20** | 1,10-Dimethylbicyclo[8.8.6]tetracosane | 151 | 1.33 | 5.82 | 23 | 164 |
| **21** | 1,10-Dimethylbicyclo[8.8.7]pentacosane | 8 | 0.55 | 6.04 | 9 | 163 |
| **6** | 1,10-Dimethylbicyclo[8.8.8]hexacosane | 32 | 1.17 | 6.23 | 19 | 170 |

[a] Found within 25 kJ of the GM at 300 K.
[b] $\Delta\kappa=\kappa_{max}-\kappa_{min}$.
[c] $\kappa_{ave}=\sum$(population-weighted $\kappa$).
[d] % Conformational compressibility=100($\Delta\kappa/\kappa_{ave}$).
[e] $\gamma_{ave}=\sum$(population-weighted $\gamma_1$+population-weighted $\gamma_2$)/2.

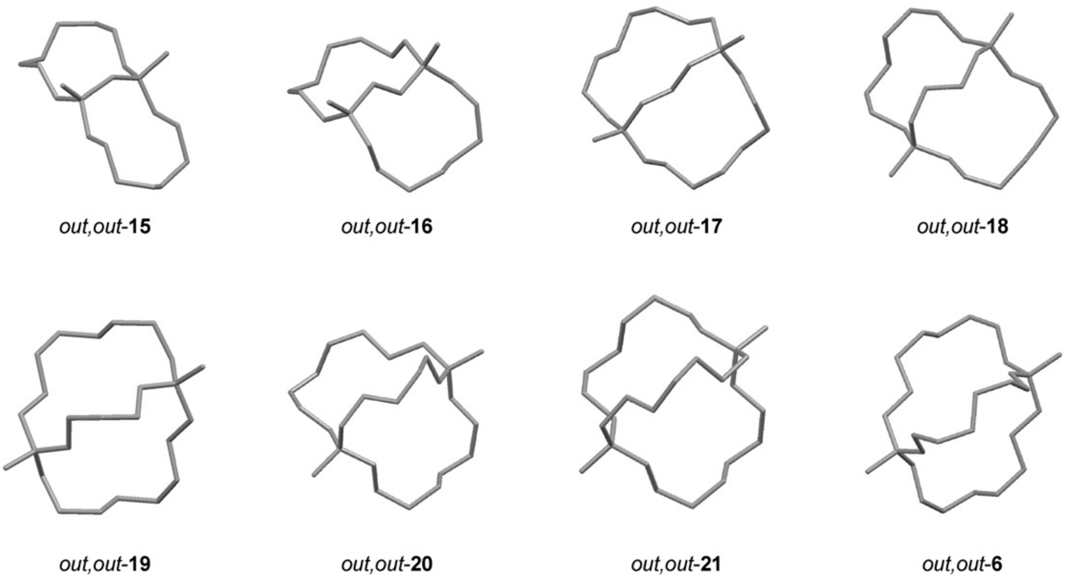

*out,out*-**15** *out,out*-**16** *out,out*-**17** *out,out*-**18**
*out,out*-**19** *out,out*-**20** *out,out*-**21** *out,out*-**6**

**Figure 4.** Global minimum energy structures (GMs) for bicycles **15**–**21** and **6**. Hydrogen atoms have been removed for clarity.

Some trends seen in the bicyclo[8.8.$n$]alkane series are in keeping with trends in the bicyclo[$m.m.m$]alkane series. All of the conformers observed possess *out,out* methyl orientations. The strain energies observed for the GMs reflect the strain associated with the primary ring (Table 4).[11] Compound **15** containing an 11-membered primary ring is the most strained, and bicycles containing progressively larger primary rings become less and less strained. However, there are trends that suggest subdivision of these compounds into three groups: compounds **15** and **16** ($n$=1 and 2, respectively), which have virtually no conformational compressibility along the inter-bridgehead axis; compounds **17**, **19**, and **21** ($n$=3, 5, and 7, respectively), which have variable bridges containing an odd number of carbons; and compounds **18**, **20**, and **6** ($n$=4, 6, and 8, respectively), which have variable bridges containing an even number of carbons.

A plot of $\Delta\kappa$ and the percent conformational compressibility versus variable bridge length ($n$) for bicyclo[8.8.$n$]alkanes **15**–**21** and for **6** for the energy window 25 kJ/mol above the respective GMs is depicted in Figure 5. In the GM of compound **15**, the bridgehead methyl carbons, bridgehead carbons, and the one-carbon bridge take up an extended *anti,anti* pentane conformation (Table 5). In compound **16**, the bridgehead methyl carbons, bridgehead carbons, and the two-carbon bridge adopt an *anti,anti,gauche* hexane conformation. These substructures have little conformational freedom, and so the inter-bridgehead distance is fixed, and compounds **15** and **16** are not very compressible along the inter-bridgehead axis. While larger bicycles possessing a variable bridge with an even number of carbons generally have greater conformational compressibility along this axis, this seems not to be the case when the variable bridge has an odd number of carbons. The number of conformers found for compounds **17**, **19**, and **21** *decreased* as the variable bridge length increased (see Table 3). In fact, the GMs for these compounds represent 27%, 97%, and >99% of the conformer populations, respectively. The dearth of conformers within 25 kJ of the latter two GMs reduces the variability of $\kappa$ and thus the magnitude of $\Delta\kappa$ and the % conformational compressibility for the [8.8.5] and [8.8.7] bicyclic systems.

**Table 4**
Global minimum energy conformers of bicyclo[8.8.*n*]alkanes **15**–**21** and **6**

| Compound | Name | Strain energy (kJ/mol) | Times GM found | % of pop[a] | $\kappa$[b] (Å) | $\gamma_1$[c] (°) | $\gamma_2$[c] (°) |
|---|---|---|---|---|---|---|---|
| **15** | 1,10-Dimethylbicyclo[8.8.1]nonadecane | 319 | 7994 | 74 | 2.83 | 132 | 132 |
| **16** | 1,10-Dimethylbicyclo[8.8.2]eicosane | 273 | 9165 | 49 | 4.04 | 100 | 129 |
| **17** | 1,10-Dimethylbicyclo[8.8.3]heneicosane | 265 | 3445 | 27 | 5.25 | 133 | 136 |
| **18** | 1,10-Dimethylbicyclo[8.8.4]docosane | 257 | 13,086 | 43 | 5.19 | 173 | 173 |
| **19** | 1,10-Dimethylbicyclo[8.8.5]tricosane | 234 | 12 | 97 | 5.94 | 143 | 143 |
| **20** | 1,10-Dimethylbicyclo[8.8.6]tetracosane | 226 | 492 | 52 | 5.91 | 156 | 168 |
| **21** | 1,10-Dimethylbicyclo[8.8.7]pentacosane | 212 | 43,469 | 100 | 6.05 | 163 | 163 |
| **6** | 1,10-Dimethylbicyclo[8.8.8]hexacosane | 202 | 3 | 73 | 6.34 | 170 | 170 |

[a] The percent of the conformer population represented by the GM at 300 K.
[b] $\kappa$ is the distance between the bridgehead carbon atoms.
[c] $\gamma$ is the angle formed by the two bridgehead carbon atoms and one methyl carbon atom.

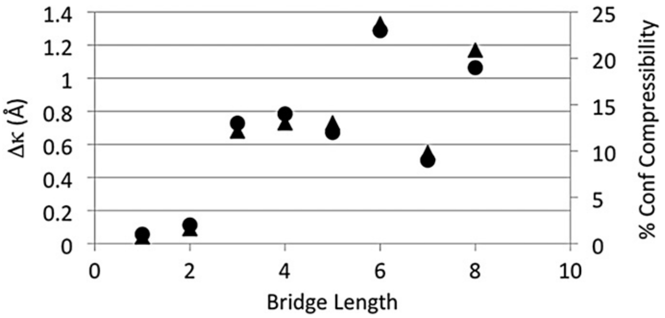


**Figure 5.** Plot of $\Delta\kappa$ (▲) and percent conformational compressibility (●) versus variable bridge length ($n$) for conformer populations within 25 kJ/mol of the GMs for bicyclo[8.8.*n*]alkanes **15**–**21** and **6**.

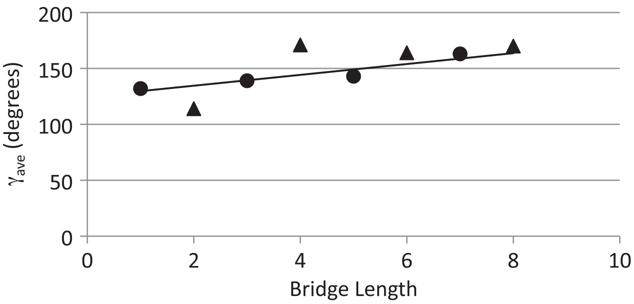


**Figure 6.** Plot of $\gamma_{ave}$ versus odd (●) and even (▲) variable bridge length ($n$) for conformer populations within 25 kJ/mol of the GMs for bicyclo[8.8.*n*]alkanes **15**–**21** and **6**. For values for odd bridge lengths, $r^2 = 0.88$

**Table 5**
Summary of torsion angles for the variable bridges in the GMs of bicyclo[8.8.*n*]alkanes **15**–**21**[a]

| Compound | Name | Number of torsions | Ratio of *anti* to *gauche* | Sequence[b] |
|---|---|---|---|---|
| **15** | 1,10-Dimethylbicyclo[8.8.1]nonadecane | 2 | 0:2 | aa |
| **16** | 1,10-Dimethylbicyclo[8.8.2]eicosane | 3 | 1:2 | aag |
| **17** | 1,10-Dimethylbicyclo[8.8.3]heneicosane | 4 | 0:4 | aaaa |
| **18** | 1,10-Dimethylbicyclo[8.8.4]docosane | 5 | 2:3 | $ag^+ag^+a$ |
| **19** | 1,10-Dimethylbicyclo[8.8.5]tricosane | 6 | 4:2 | $g^-ag^+g^+ag^-$ |
| **20** | 1,10-Dimethylbicyclo[8.8.6]tetracosane | 7 | 4:3 | $ag^+ag^+g^+ag^-$ |
| **21** | 1,10-Dimethylbicyclo[8.8.7]pentacosane | 8 | 4:4 | $ag^+ag^+g^+ag^+a$ |

[a] The torsions mapped extend from one methyl carbon, through the bridgehead, along the variable bridge, through the second bridgehead, to the second methyl carbon.
[b] a=*anti*, $g^+$=*gauche* plus, $g^-$=*gauche* minus.

For compounds **15**–**21**, the angles $\gamma_1$ and $\gamma_2$ are also of interest. It was anticipated that, as the length of the variable bridge ($n$) is increased, these angles would smoothly increase and approach 180°. For odd values of n, a positive correlation ($r^2$=0.88) does exist between $n$ and the population-weighted average angle, $\gamma_{ave}$ (see Fig. 6). Restriction of **15** to the *anti*,*anti* pentane conformation (see Table 5) constrains $\gamma_{ave}$ to a minimum value (for the odd series). As $n$ increases, the distance spanned and the conformational freedom of the variable bridge increase, as does $\gamma_{ave}$, while torsional symmetry along the bridge is maintained (Table 5). Restriction of **16** to the *anti*,*anti*,*gauche* hexane conformation constrains $\gamma_{ave}$ to a minimum value (for the even series). Unexpectedly, values of $\gamma_{ave}$ for **18**, **20**, and **6** cluster around 170° (Fig. 6). As $n$ increases, the distance spanned and the conformational freedom of the variable bridge increase. However, the variable bridges in these compounds possess odd numbers of torsions, numbers of *anti* and *gauche* torsions that differ by one, and often lack torsional symmetry along the variable bridge (Table 5). It appears that the [8.8.4], [8.8.6], and [8.8.8] systems all possess sufficient conformational freedom to permit $\gamma_{ave}$ to closely approach 180°.

## 3. Discussion

Polymers that contain rigid 'linear spacers', such as bicyclo[1.1.1]pentane or bicyclo[2.2.2]octane, are generally insoluble.[14,15] We postulated several years ago that incorporation of larger 'linear spacer' bicycles would render the polymers more soluble, and fibers formed from such polymers more elastic, when compared with polymers constructed from rigid materials. At that time, compounds **6** and **7** were identified as synthetic targets, since proof was needed that *out*,*out*-bicyclo[8.8.8]hexacosanes bearing substituents at the bridgeheads could be prepared. Serendipitously, direct evidence of conformational compressibility along the inter-bridgehead axis was obtained in a single case by X-ray crystallographic analysis of **7**.[8] In the present work, examination by Monte Carlo conformational searching of a large set of bicyclo[*m*.*m*.*m*]alkanes where $m$=1–10 suggests that significant conformational compressibility will exist along the inter-bridgehead axis for sufficiently large bicycles, and that the % conformational compressibility will increase with increasing $m$. Given our interest in the use of bicyclo[8.8.8]hexacosanes as molecular springs, it is worthwhile noting that (1) the % conformational compressibility of **7** along the inter-bridgehead axis among the four conformers observed in the crystal was 15%,[8] while the calculated % conformational compressibility of **7** was 47% (considering the much larger set of conformers within 50 kJ of the GM); (2) the conformer of **6** and the four conformers of **7** observed in the crystal structures were all found in the conformational searches; (3) the average inter-bridgehead distances ($\kappa_{ave}$) for **6** and **7** were approximately 6 Å, a value similar to the long axis of a benzene ring. This last feature suggests modification of the structure of Kevlar® by from partial to substantial replacement of benzene-containing monomers with bicyclo[8.8.8]hexacosane-containing monomers. Such materials might retain high tensile strength, be more processable, and/or allow better distribution of the force of impact. Syntheses of monomers related to **6** and **7** are currently in progress.

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## Supplementary data

Details of the Monte Carlo searches and graphical representations of the distribution of conformers with respect to $\kappa$ and strain energy at 300 K for each of the bicycles studied. This material is available free of charge via the Internet. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2009.10.022.

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