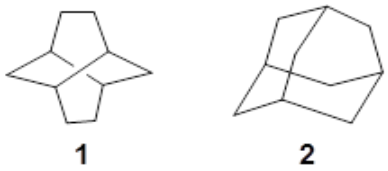
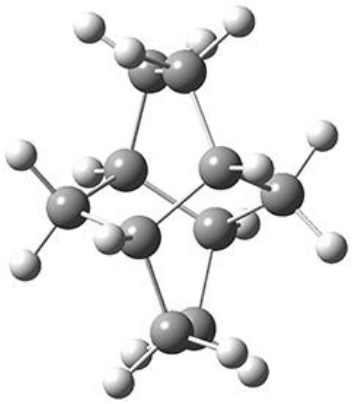
POLYTWISTANE!

Twistane **1** is a more strained isomer of adamantane **2**. The structure of **1** is shown in Figure 1.





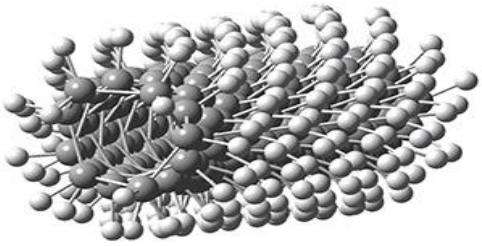
1

Figure 1. B3LYP/6-31G(d) optimized structure of **1**.

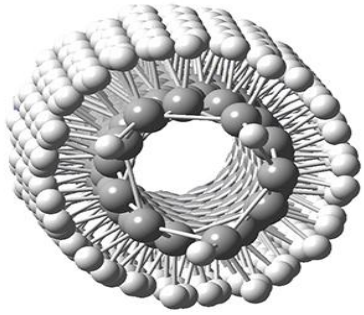
Adamantane is the core structure of diamond, which can be made by appending isobutene groups onto adamantane. In an analogous fashion, twistane can be extended in a linear way by appending ethano groups in a 1,4-bridge. Allen, Schreiner, Trauner and co-workers have examined this “polytwistane” using

computational techniques.[1] They examined a $(CH)_{236}$ core fragment of polytwistane, with the dangling valences at the edges filled by appending hydrogens, giving a $C_{236}H_{242}$ compound. This compound was optimized at B3LYP/6-31G(d) and shown in Figure 2a. (Note that I have zoomed in on the structure, but by activating Jmol – click on the figure – you can view the entire compound.) A fascinating feature of polytwistane is its helical structure, which can be readily seen in Figure 2b. A view down the length of this compound, Figure 2c, displays the opening of this helical cylinder; this is a carbon nanotube with an inner diameter of 2.6 Å.

(a)



(b)



(c)

Figure 2. B3LYP/6-31G(d) structure of the $C_{236}H_{242}$ twistane. (a) A zoomed in look at the structure. This structure links to the Jmol applet allowing interactive viewing of the molecule – you should try this! (b) a side view clearly showing its helical nature. (c) A view down the twistane showing the nanotube structure.

Though the molecule looks quite symmetric, each carbon is involved in three C-C bonds, and each is of slightly different length. The authors go through considerable detail about addressing the symmetry and proper helical coordinates of polytwistane. They also estimate a strain energy of about 1.6 kcal mol^{-1} per CH unit. This modest strain, they believe, suggests that polytwistanes might be reasonable synthetic targets.

Source: http://comporgchem.com/blog/?p=3126