From Benzene to Nanothreads: intermediate polymers and topological pathways

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An Energy Frontier Research Center

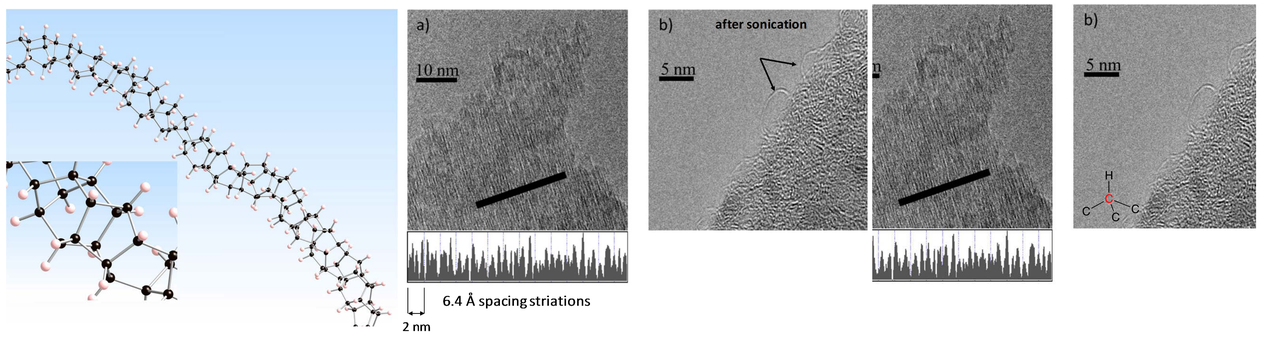
EFree Project: New Nanophase Carbons

Goal: *To stabilize and characterize new forms of carbon through tailored synthetic processes for the development of new structural materials.*

Synthesis and characterizations of nanothreads

Experimental studies of benzene compression date back a century. However, only amorphous products with no clearly discernible order had been observed. Recently, the Penn State group has for the first time recovered ordered products in slow decompression of benzene from 20 GPa. The partially crystalline products comprise one-dimentional sp^3 CH nanothreads (Figure 1).

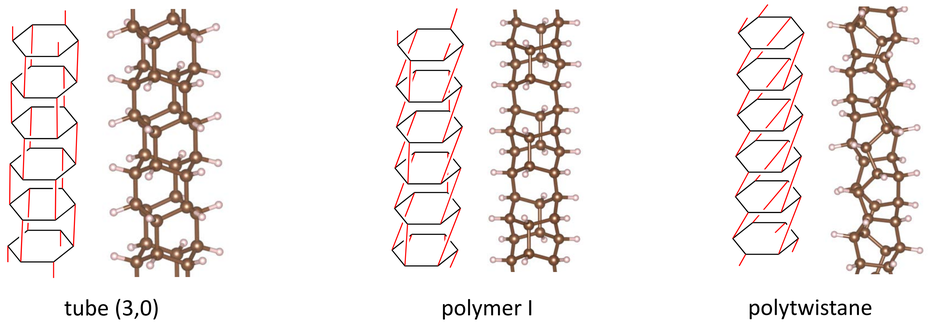
Figure 1. *A model of nanothread, Transmission electron microscopy (TEM) images and pair distribution functions*



Enumerating possible nanothread structures

We enumerated the possible distinct carbon nanothreads that can be formed by the one-dimensional stacking of benzene molecules in the solid state. The structural constraint applied to enumeration of the nanothreads is that each benzene ring must have six covalent bonds to next neighbor benzene rings in each direction along the length of the thread. With a maximum of two benzene molecules per topological unit cell ($Z_{topo} \leqslant 2$), a total of 50 distinct nanothreads is possible. Figure 2 shows three low energy structures that had been suggested before.

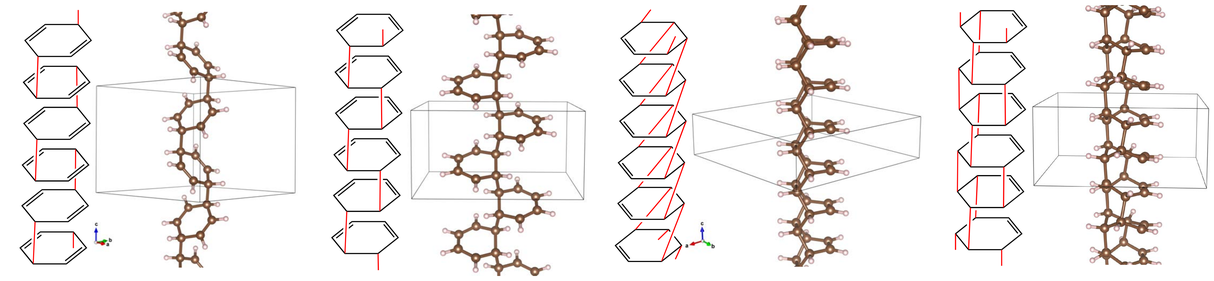
Figure 2. *Three of the 50 distinct nanothreads enumerated*



Enumerating possible intermediate polymer structures

On the way to the completely saturated nanothreads one may have linear benzene polymers with some unsaturation remaining, either one (degree-four) or two (degree-two) double bonds per ring. We enumerated these as well, obtaining 8 + 23 isomers. Figure 3 shows two structures for each type of intermediate polymers.

Figure 3. *Two degree-two and two degree-four intermediate polymer structures*



Topological pathways from benzene to nanothreads

With the data base of structures of degree-two, degree-four and degree-six polymers, we compared their relative energies to other $(CH)_n$ species, including benzene, benzene dimer and graphane A (Figure 4). We also examined all possible topological pathways from benzene to nanothreads via intermediate polymers. Figure 5 shows two such pathways leading to polytwistane and tube(3,0).

Figure 4. *Energies diagram of $(CH)_n$*

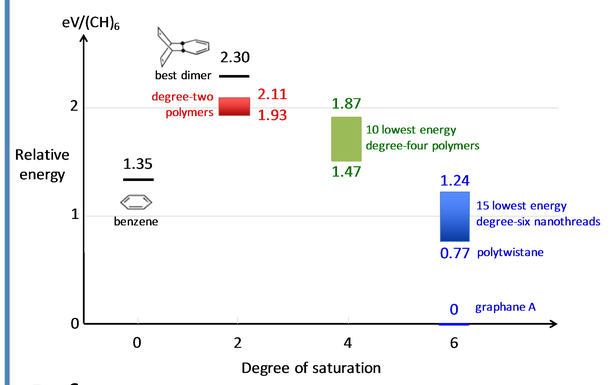
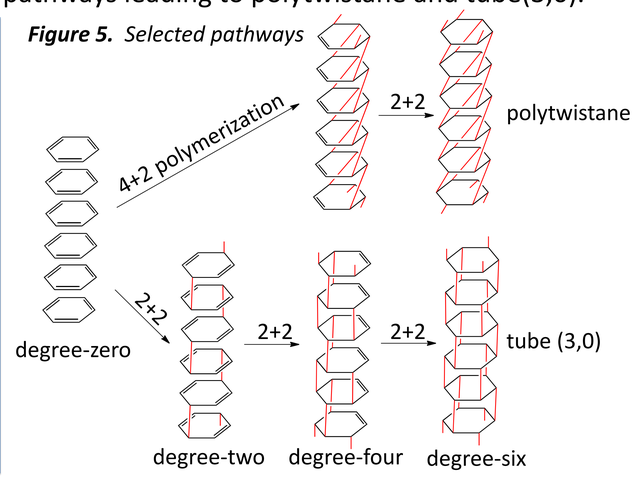


Figure 5. *Selected pathways*



References

1. Fitzgibbons, T.C., Guthrie, M., Xu, E.-S., Crespi, V.H., Davidowski, S.K., Cody, G.D., Alem, N., & Badding, J.V., Benzene-derived carbon nanothreads. *Nat. Mater.*, **14**, 43 (2015).

2. Xu, E.-S., Lammert, P.E. and Crespi, V.H. Systematic Enumeration of sp^3 Nanothreads. *Nano Lett.*, **15**, 5124 (2015).

3. Chen, B., Hoffmann, R., Ashcroft, N.W., Badding, J.V., Xu, E.-S., Crespi, V., Linearly polymerized benzene arrays as intermediates, tracing pathways to carbon nanothreads. *J. Am. Chem. Soc.*, DOI: 10.1021/jacs.5b09053

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