Mechanical Properties

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Harder than Diamond: Determining the Cross-Sectional Area and Young's Modulus of Molecular Rods

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The rapidly growing area of nanotechnology has provoked much interest in the various moduli of elementary building blocks at the nano/molecular level. Among these moduli, the most frequently discussed is probably Young's modulus, and we describe here the derivation of Young's modulus for two molecular rods, namely polyynes (**1**) and [*n*]staffanes (**2**, poly-1.1.1-propellanes; see Figure 1)[1].

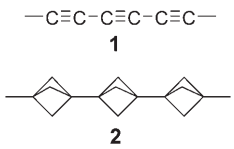

Figure 1. Sections from polyyne (**1**) and [*n*]staffane (**2**).

Given the force applied to a structure, Young's modulus (Y) can be calculated provided the area (A) to which force is applied is known. This, of course, is in addition to the deformation (ΔL) in the length (L) according to Equation (1).[2]

$$\frac{F}{A} = \frac{Y\,\Delta L}{L} \tag{1}$$

In the case of longitudinal compression of a solid homogeneous rod, the effective cross-sectional area (CSA) is the physical cross-sectional area of the rod. However, in the case of a unidimensional molecular rod such as polyyne, the effective cross-sectional area is not easily defined. The definition must rest heavily on our understanding of the nature of matter. In most cases, matter is associated with mass, therefore if the force is exerted on the mass, then the relevant dimension would be the cross-sectional area of the carbon nucleus. On the other hand, since any physical contact, including a punch thrown in a boxing ring, is in fact an interaction between electron clouds, one should consider the CSA of the electron cloud. It is, however, "already apparent from the nature of the wavefunction for atoms and ions that

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they have no definite size."[3] Thus, the radius, like the partial atomic charge in polar molecules, although intuitively a very appealing concept, is not physically observable. Moreover, it is difficult to justify the use of any of the commonly applied radii such as the ionic, covalent, or the van der Waals radii for the electronic cloud in this context.

In the present work we have succeeded in calculating the effective cross-sectional area and the Young's modulus of a polyyne molecular rod using a combination of quantum mechanical and classical mechanical engineering tools. Our approach is based on the fact that longitudinal compression of a rod will eventually lead to its buckling. As we know that the larger the cross-sectional area of the rod the more it will resist buckling, there must be a correlation between the critical point of the collapse (buckling) and the surface area of the rod. This investigation was performed using the following procedure: In the first step, the structure and the energy of a given polyyne was calculated using the Gaussian 03 program at the B3LYP/6-31G level.[4] Next, the fixed distance between the two terminal carbon atoms was gradually reduced and the energy was optimized at each step with respect to the other structural parameters. These data were inserted into Equation (1), where F is the derivative of the energy (E) with respect to L (the distance between the two terminal carbons in the unconstrained system), and ΔL is the change of this distance upon going to the constrained structure, to give YA. This is the analog to a unidirectional loading of a rod in mechanical engineering terminology.

Further compression of the rod leads to buckling. At the onset of buckling we have the Euler relation [Eq. (2)],[5] which is the solution for a simply supported column under compression.

$$F = \frac{\pi^2 Y I}{L^2} \tag{2}$$

In this equation, I is the minimal static moment of inertia. YI can be calculated from this equation. The square root of the ratio YI/YA ($=I/A$) is equal to the radius of gyration, ρ, which in turn is equivalent to half of the radius, r, of the rod. r, Y, and I are given for a series of polyyne molecular rods in Table 1.

It should be pointed out that the values in Table 1 are not exact since they contain the approximations assumed in the mechanical engineering equations and the approximations used in the various definitions, in addition to the fact that the structure optimization was done using the default parameters of the Gaussian program. Regarding the definitions used, the buckling point was defined as the point at which one of the CCC angles decreased below 179°, and the energy before the critical point for Equation (1) was taken uniformly to be 0.1 % of the original length of the rod. The energy after the buckling was taken at a compression of 0.1 Å from this point. A change in these definitions, such as taking the buckling point as the geometry at which one of the CCC angles crossed the 178° value, rather than 179°, or varying the distances mentioned above by 50 %, changed the final value of the radius by less than 4 %. The direction of the buckling is governed by minor differences in the significant figures of the forces in the perpendicular directions.

It should be noted that the sensitivity to the basis set is rather low. The radius of the C_{10} polyyne was also calculated after addition of diffuse functions or d orbitals and the values obtained were 0.34 and 0.36 Å, respectively, instead of 0.35 Å.

An alternative method to calculate YI is by replacing the "buckling method" (first method in Table 1) with one based on a bending mode (Figure 2). Here, the two terminal carbons

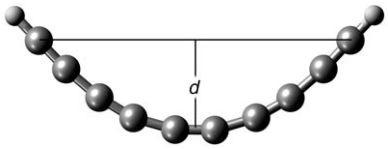

Figure 2. Bending mode for a C_{10} polyyne rod.

are restricted to a given axis and the center of the rod is forced to a point below this axis. The relation between YI and d for a small deformation is given by Equation (3)[6].

$$YI = \frac{F L^3}{48\, d} \tag{3}$$

Again, the aforementioned combination of YI and YA yields the effective radius of the rod. The data obtained using this procedure are also given in Table 1 (second method). The close resemblance of the two sets of values, in spite of the approximations involved in the mechanical engineering equations, is highly encouraging.

Thus, a physical parameter that was previously considered unobservable is quantitatively determined here. It is worth noting that we have obtained the cross-sectional area of the rod by interweaving two entirely different methodologies, none of which contains, either implicitly or explicitly, any value related to the effective radius of the rod. It is left for future studies to see how this value relates to the various π and σ components of the electronic wavefunctions.

An immediate outcome of this result is, of course, that if the cross-sectional area of a carbon atom in a nanotube, for example, is anywhere near that of our molecular rod the Young's modulus calculation for nanotubes[7] should be corrected accordingly.

Table 1: Radius, Young's modulus, and the static moment of inertia for polyyne rods (HC_mH, $m = 4$–20) calculated by the two methods.

	First method			Second method		
m	Radius [Å]	$Y\times10^{-13}$ [N m^{-2}]	$I\times10^{42}$ [m^4]	Radius [Å]	$Y\times10^{-13}$ [N m^{-2}]	$I\times10^{42}$ [m^4]
4	0.35	4.37	1.24	0.31	5.72	0.72
6	0.36	3.95	1.32	0.36	4.05	1.25
8	0.35	3.95	1.23	0.34	4.33	1.03
10	0.36	3.73	1.30	0.33	4.36	0.95
12	0.34	4.38	1.10	0.32	5.20	0.78
14	0.35	4.09	1.19	0.32	4.87	0.84
20	0.35	3.91	1.25	0.33	4.55	0.92
Av.	0.35 ± 0.005	4.0 ± 0.2	1.23 ± 0.07	0.33 ± 0.02	4.7 ± 0.6	0.9 ± 0.2

Another interesting outcome of this study is the actual value of the Young's modulus of the acetylenic rod (Table 1). It turns out that our calculated Y is around 40 times larger than that of the hardest known material—diamond—whose Young's modulus is 1063 GPa ($Pa = N m^{-2}$).[8] The observed Young's modulus of a material is usually a result of the Young's modulus of the molecules of which it is comprised, their relative alignment, and the intermolecular voids. Since diamond can be viewed as a single molecule, having results for these two molecules provides, for the first time, an opportunity to examine the connection between Young's modulus and basic molecular parameters. A major difference between diamond and polyyne is the strength of the bonds involved. While the bonds in the latter are sp fortified by π bonding, the carbon atoms in diamond are interconnected by a series of much weaker sp^3-hybridized bonds. Although the issue is somewhat controversial, it seems that polyyne enjoys further strengthening due to conjugation, which is absent in diamond.[9] The hardness of the acetylenic rod stems, therefore, from the steeper potential functions of the bond, where a small compressional motion along its longitudinal axis results in a sharp rise in energy, namely higher resistance to a change in the position of the nuclei.

Since diamond has a three-dimensional network of bonds it is difficult to carve a unidirectional rod from it. One would like to simulate a rod of diamond in the sense of having a core repeating unit of the rod consisting of sp^3-hybridized carbon atoms, and [*n*]staffanes **2** seem to serve as a close model for this purpose. All carbons in the 1.1.1-bicyclopentane unit have a hybridization ranging from $sp^{3.3}$ to $sp^{2.5}$ for the internal C–C bonds, whereas the hybridization of the external bond has a somewhat lower p character ($sp^{2.1}$). Like in diamond, all four bonds of the carbon atoms along the axis of the rod participate in resisting deformation. The degree of flexibility that is acquired by bond-angle deformation in the bridges can also be found in diamond. Consequently, we have calculated the effective radius, Y, and I, using the compression/buckling method, for rods consisting of three and four bicyclopentane units, assuming that they will display a hardness similar to that of diamond.

Table 2: Radius, Young's modulus, and the static moment of inertia for [*n*]staffane rods.

n	Radius [Å]	$Y \times 10^{-12}$ [$N m^{-2}$]	$I \times 10^{41}$ [m^4]
3	0.78	4.9	2.9
4	0.73	5.6	2.3
Av.	0.76 ± 0.02	5.3 ± 0.3	2.6 ± 0.3

The data presented in Table 2 show, as expected, that the [*n*]staffanes' Young's modulus is close to that of diamond (around five times larger) and that its effective radius (approximating it to be a cylindrical rod) is, as expected, larger than that of a rod comprised of acetylene units.

As regards Young's modulus, one can conclude that, since among the sp-, sp^2-, and sp^3-hybridized bonds the sp^3 bond of diamond is the weakest one, some organic compounds may display a rigidity higher than that of diamond, although only along a single axis. The uniqueness of diamond stems from the fact that it displays the same strength in all directions. On the other hand, the uniqueness of polyyne is explained by the fact that it consists of the strongest bonds among the three groups of hybridization and therefore we expect that it will be very difficult to break its record in hardness, at least within the realm of carbon-based rods.

In light of the fact that no material significantly stronger than diamond has been synthesized up to now,[10] a very interesting option in three dimensions is a diamond in which two carbon atoms are connected not by a σ (sp^3) bond but by an acetylenic unit.[11] The building block of such a structure—triethynylmethane $C(C{\equiv}CH)_4$—was successfully synthesized[12] and studied computationally.[13] Although it is likely that the large voids in the "yne diamond" will take their toll on the overall hardness, it is possible that the large difference in the nature of the constituent bonds will more than overcome this deficiency. Although the hybridization of the corner carbon atoms remains sp^3, the sp^3–sp bond is significantly stronger than the sp^3–sp^3 bond and, as was shown recently by Schleyer and Houk,[9a] this bond is further stabilized by the neighboring triple bond. The internal radius of the adamantane cavity in the yne-diamond is about 2.16 Å (3.86 Å less the van der Waals radius of carbon). Chelation of an inert gas atom of the right size in this cavity will no doubt overcome the aforementioned problem of the internal voids. Based on its van der Waals radius, Xe ($r = 2.16$ Å) seems to be the element of choice (Figure 3). The synthesis of the yne-diamond is, however, an immense task to fulfill, and filling its yne-adamantane cavities with Xe, which will significantly increase its stiffness,[14] is also a colossal challenge.[15]

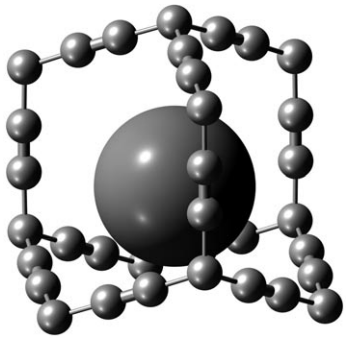

Figure 3. Yne-adamantane unit of yne-diamond containing a Xe atom. The size of the carbon atoms has been reduced to enable a better view.

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[14] Young's modulus is, in fact, the measure of stiffness that is commonly referred to as hardness. However, in materials science, hardness is measured as the deformation caused by the indenting tip. Yet, hardness and Young's modulus are closely related, and diamond has the highest known Young's modulus.
[15] Computational data are given in the Supporting Information.

