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Auxetics at the Molecular Level: A Negative Poisson's Ratio in Molecular Rods

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Auxetic materials are materials that, counterintuitively, become thicker when stretched and thinner when compressed (negative Poisson's ratio). Examples found up to now have been based mainly on the microgeometry of the material. Using quantum mechanical computations we have identified the first molecular systems, poly[*n*]prismanes ($n = 3$–6), that manifest auxetic behavior at the molecular level. The magnitude of the negative Poisson's ratio in these prismanes ranges from 7 to 15%.

Most materials become thinner when longitudinally stretched and thicker when compressed; that is, they have a positive Poisson's ratio. The latter is defined as the ratio of a lateral contraction to the longitudinal extension during the stretching of a material.[1] Normally, a Poisson's ratio ranges between 0.2 and 0.5. The cork stopper used in wine bottles is an example of a material having a near-zero Poisson's ratio. This characteristic is essential because, otherwise, when pressed against the bottle the cork would have to become thicker, making the seal impossible. In 1987, the first material with a negative Poisson ratio (now called an auxetic material[2]), a foam, was reported by Lakes.[3] The new horizons that were opened by the discovery of auxetic materials induced a major upsurge in structural engineering technologies, with uses ranging from nuclear reactors to the fixing of walls of blood vessels.[4]

The major cause for a negative Poisson's ratio is the microstructure of the material (inverted honeycomb geometry, etc.).[4] It has been suggested that a solid with a porosity of less than 40% cannot be auxetic unless the solid is intrinsically auxetic at the molecular level.[5] Needless to say, high porosity may impair many applications because of low strength and so on. Yet, no molecule is so far known to display auxetic behavior. Herein, we report that molecular rods with a prismanic structure provide the first case of auxetic behavior at the molecular level. It should be pointed

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out that in addition to foams, a negative Poisson's ratio has been reported for certain crystals[6] in specific directions and is also predicted for extreme states of matter such as the cores of white dwarfs and the outer crusts of neutron stars.[7]

The equilibrium structure and the effect of stretching and compressing various prismanic rods were computed using quantum mechanicals. The procedure follows very closely the one we have recently used.[8] The common feature displayed by all the prismanes is that while the two end rings exhibit normal behavior, the internal rings are auxetic. Namely, they expand upon stretching and contract upon compression. The computations were performed at the B3LYP/6-31G* level using the Gaussian 03[9] program. In the first step, each rod structure was fully optimized. Then, the distance between the corresponding atoms on the two capping rings were fixed at a given length, either shorter (compression) or longer (stretching), and all the other degrees of freedom were reoptimized with respect to the energy. The strained structures were found to have only positive frequencies. The auxetic behavior was found to be independent of method and basis set since sample calculations using AM1, B3LYP/6-31G, MP2/6-31G*, BPW91/6-31G*, and B3LYP/6-311G(2df,2p) all revealed the same phenomenon (Supporting Information).

In Figure 1, the ring bond lengths of deca[3]prismane[10] are plotted as a function of the percent change in the length of the molecular rod. The Poisson's ratio calculated for the

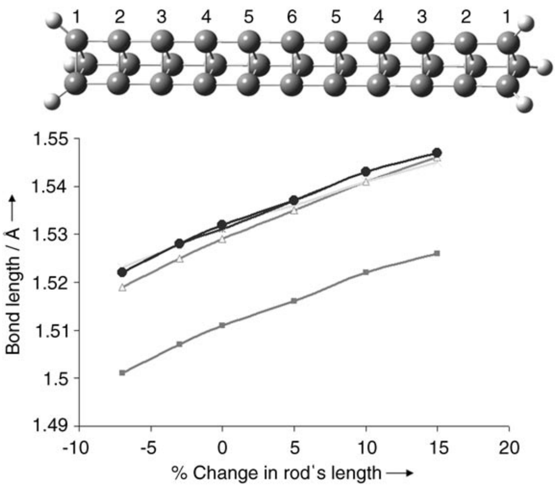


Figure 1. Variation in the internal cyclopropane bond length as a function of the percent change in the length of deca[3]prismane (numbering is according to the scheme shown). The upper group of lines is for rings numbered 3, 4, 5, and 6, the lower line is for ring number 2. The length of the fully optimized rod is 16.001 Å.

internal rings varies from −7% to −9% and averages −7.5%. Figure 1 shows that the Poisson's ratio over the whole range of rod length (−7% to +15%) is remarkably constant, despite the large change of energy involved (up to 300 kcal mol^{-1} for the 15% stretching). As mentioned before, the capping rings (numbered 1 in Figure 1) have a normal Poisson's ratio whereas all the nine internal rings have a negative ratio.

The constancy of this auxetic effect for the internal rings is remarkable when compared to the various porous foams. Using the two-dimensional classical example of reenterant honeycomb (Figure 2),[2] it is clear that the auxetic effect will initially be large and will gradually decay as the dent in the hexagon flattens out.

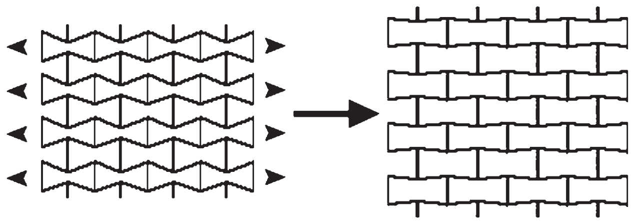
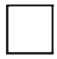


Figure 2. A two-dimensional model for a reenterant honeycomb.

In Table 1, the average Poisson's ratio over all the internal rings is given for a series of prismanes with different numbers of rings as a function of length of the rod. These values were

Table 1: Average Poisson's ratio over all the internal rings for a series of prismanes over the range 97%–105% (energies are given in the Supporting Information).

No. of rings				
3	−0.071	−0.066	−0.115	−0.133
4	−0.081	−0.079	−0.131	−0.156
5	−0.083	−0.079	−0.112	
6	−0.078	−0.064	−0.091	
7	−0.075			
8	−0.081			
9	−0.077			
10	−0.068			
11	−0.073			
Averages:	−0.076	−0.072	−0.112	−0.144

determined over the range 97%–105% (for the sake of simplicity, since the rods are not cylindrical and two radii can be attributed to them, the C–C bond length was used for the calculation of the Poisson's ratio; this procedure yields results very close to a Poisson's ratio based on each of the radii).

The data show that [3]- and [4]prismanes (based on cyclopropane and cyclobutane, respectively) have nearly the same auxetic effect, whereas the rods consisting of cyclopentane and cyclohexane rings display a significantly higher effect culminating in [6]prismane with four rings, which has a negative Poisson's ratio of 15%. Interestingly, in spite of their nonplanar geometry, cyclohexane and cyclopentane are fully planar in the derived prismanes.

An unresolved conundrum is the origin of this phenomenon. It is certainly not a result of some sort of internal compensation between the contraction of the two external rings and the expansion of the inner ones. This cause can be ruled out because the Poisson's ratio of the inner rings

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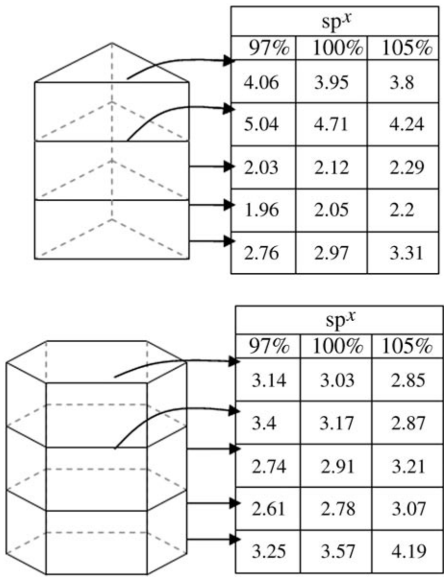
remains constant (see Figure 1) regardless of the length of the rod (the number of the rings in the rod) while the contraction of the two external rings is also constant (0.053 ± 0.007) over the whole range of rod length (Supporting Information). One would expect that the expansion of the rings would be accompanied by an increase in the p-orbital character in the bonds within the rings. Surprisingly, NBO analysis shows that upon stretching, the s component increases for bonding within the ring while the interlayer bonds become enriched with the p component. Examples of the changes in hybridization upon stretching and compression are given in Figure 3 for tri[3]prismane and tri[6]prismane.



sp^x		
97%	100%	105%
4.06	3.95	3.8
5.04	4.71	4.24
2.03	2.12	2.29
1.96	2.05	2.2
2.76	2.97	3.31

sp^x		
97%	100%	105%
3.14	3.03	2.85
3.4	3.17	2.87
2.74	2.91	3.21
2.61	2.78	3.07
3.25	3.57	4.19

Figure 3. Variation of the p character (*x*) in the bonds of tri[3]prismane and tri[6]prismane as a function of the percent of stretching (105%) or compression (97%).

It is interesting to note that the normal Poisson's ratio of the capping rings increases also with the ring size. Its value is 0.053, 0.097, 0.126, and 0.15 for the [3]-, [4]-, [5]-, and [6]prismanes, respectively.

These molecular rods display an additional interesting feature. Namely, in spite of the differences in the sizes of the rings, and therefore in the nature of the bonds within the rings which affects the hybridization of the bonds connecting the rings along the rod, the energy for stretching these rods is proportional to the number of bonds stretched, regardless of the size of the rings they connect. This aspect is demonstrated in Figure 4 for a stretching of 5%. The slope of the line is about 1.44 kcal mol^{-1}. Thus, stretching of tetra[3]prismane (with $4 \times 3 = 12$ interlayer connecting bonds with a hybridization of sp$^{2.15}$ each; NBO analysis) and tri[4]prismane (with $3 \times 4 = 12$ interlayer connecting bonds with hybridization of sp$^{2.34}$ each; NBO analysis) by 5% produces the same energy cost (ca. 21 kcal mol^{-1}).

More than 30 years ago, Woodward and Hoffman referred to prismanes as "an angry tiger unable to break out of a paper cage."[11] Indeed, except for the basic ones,[12] not very many have been synthesized. We hope that our findings will catalyze the efforts in this direction.

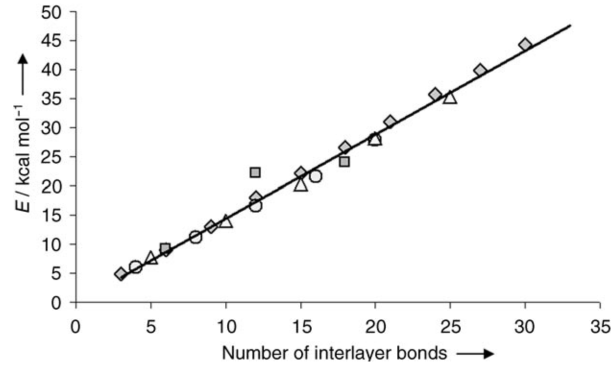


Figure 4. Energy needed to stretch various [*n*]prismanes by 5% as a function of the number of bonds connecting the layers; diamonds: [3]prismane; circles: [4]prismane; triangles: [5]prismane; squares: [4]prismane.

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