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Self expanding molecular networks

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A series of polyphenylacetylene networks are modelled through force-field based simulations and are predicted to exhibit unusual mechanical properties, namely, negative Poisson's ratios (auxetic), a property which is explained through a simple model involving a network of connected rotating triangles.

Materials with a negative Poisson's ratio [auxetic, see methods section, eqn. (2)] exhibit the unexpected property of becoming wider when stretched and thinner when compressed.[1,2] Apart from the purely scientific importance of having such an unusual basic property, a negative Poisson's ratio gives a material many additional beneficial effects,[2,3] such as increased shear stiffness, increased plane strain fracture toughness and increased indentation resistance. Auxetics also have a natural ability to form synclastic doubly curved surfaces (*i.e.* dome shaped). This means that auxetic materials are superior to conventional counterparts in many practical applications. Unfortunately, although several auxetics have now been discovered or manufactured (*e.g.* foams,[3] microporous polymers[4] and silicates[5]), a negative Poisson's ratio is not a common feature in most everyday materials (*e.g.* the Poisson's ratio of most isotropic polycrystalline metals is approximately +0.3).

In recent years, considerable attention has been focused towards designing and synthesising molecular auxetics.[2,6] Such systems would offer the advantage over naturally occurring auxetics that they can be 'made to measure' to have a predefined set of mechanical properties.

In this communication we present a new class of molecular auxetics that have been predicted to exhibit negative Poisson's ratios.† They may be described as parallel 'graphite-like' layers each containing a planar polyphenylacetylene infinite network. These planar networks are a tessellation of a repeat unit having two equilateral molecular triangles at 60° to each other, an example of which is illustrated in Fig. 1(*a*). Homologues of the network in Fig. 1(*a*) may be produced by using longer or shorter acetylene chains. Since there is no simple way of naming these polytriangular networked systems, we shall henceforth refer to them as polytriangles-*n*-yne where *n* refers to the number of triple bonds per acetylene chain. Thus the network in Fig. 1(*a*) shall be referred to as polytriangles-2-yne.

Molecular mechanics simulations of these systems (aligned as in Fig. 1) using Cerius^2 V3.0 (Molecular Simulations Inc., San Diego, USA) have shown that the minimum energy separation between the different layers is approximately 3.6 Å, a distance which indicates the π–π interactions in between the different layers are being well represented. As illustrated in Table 1, it was observed that for $n \geqslant 2$, these polytriangles-*n*-yne networks exhibit negative Poisson's ratios (auxetic) in the Ox_2–Ox_3 plane (*i.e.* negative ν_{23} and ν_{32}) which tend to -1 as n increases. Furthermore, for $n \geqslant 2$, all the six Poisson's ratios were predicted to be negative. This is the first time that a material is predicted to simultaneously exhibit six negative mutually orthogonal Poisson's ratios.

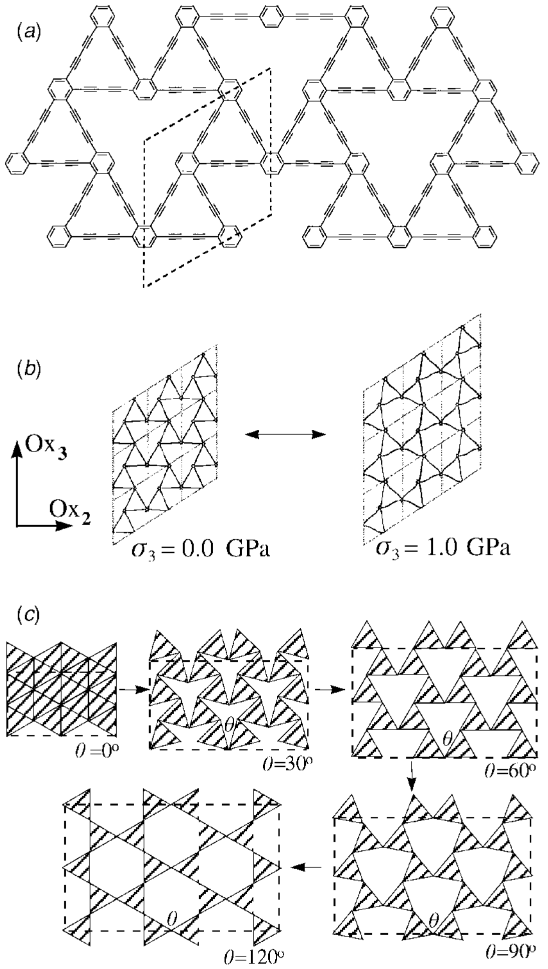

Fig. 1 (*a*) The structure of polytriangles-2-yne; (*b*) the minimum energy configurations of polytriangles-7-yne at $\sigma_3 = 0.0$ GPa and at $\sigma_3 = 1.0$ GPa; (*c*) the concept behind the design of the molecular networks: the idealised 'rotating triangles' networks. The molecular networks relate to the structure where $\theta = 60°$.

Table 1 The predicted single crystalline Poisson's ratios (ν_{ij}) of the polytriangles-*n*-yne where *n* is the number of triple bonds in the acetylene chains. The Ox_i axis are as defined in Fig. 1

n	ν_{12}	ν_{21}	ν_{31}	ν_{13}	ν_{23}	ν_{32}
1	+0.01	+0.10	+0.06	+0.01	+0.23	+0.19
2	−0.01	−0.02	−0.02	−0.01	−0.43	−0.43
3	−0.05	−0.27	−0.22	−0.04	−0.71	−0.72
4	−0.01	−0.01	−0.01	−0.01	−0.83	−0.83
5	−0.01	−0.01	−0.01	−0.01	−0.90	−0.90
6	−0.07	−0.14	−0.16	−0.08	−0.94	−0.93
7	−0.08	−0.12	−0.14	−0.09	−0.96	−0.95
8	−0.09	−0.11	−0.12	−0.10	−0.97	−0.96

In an attempt to understand the reason behind these very unusual properties, especially the very highly negative ν_{23} and ν_{32}, the minimum energy configurations at different loads in the Ox_2 and Ox_3 directions were obtained. From these minimum energy configurations, it was observed that for the larger triangles, the main type of deformation mechanism is through flexure of the acetylene chains. This flexure results in an overall

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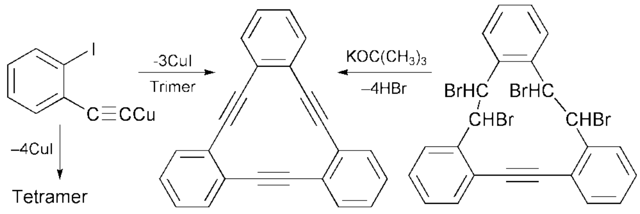

Scheme 1 The synthesis of single triangles.[11]

relative rotation of the triangles as illustrated for $n = 7$ in Fig. 1(*b*).

The possibility of achieving negative Poisson's ratios *via* rotating triangles compliments the recent predictions that a number of zeolites deform though a 'rotating squares' mechanism[7,8] and hence produce negative Poisson's ratios.[7–10] As illustrated in Fig. 1(*c*), a two dimensional structure composed of rigid hinged equilateral triangles connected together through hinges is geometrically constrained to maintain its aspect ratios and hence have in-plane Poisson's ratios of -1.[8] This simple geometric model explains why for the larger networks (*i.e.* the ones where the geometry of the triangles become more conspicuous), the Poisson's ratio tends to -1. The other four negative Poisson's ratios are probably due to a variation in the amount of interactions between the different layers.

Finally, we note that other similar two-dimensional delocalised π-systems such as graphyne and graphdiyne (*i.e.* the all-carbon fully substituted versions of polytriangles-1-yne and polytriangles-2-yne respectively) have also attracted considerable attention *vis-à-vis* their unique optical and electronic properties.[10] Unfortunately, graphyne and graphdiyne do not exhibit any auxeticity as they lack the required polytriangles geometry.[8] We also note that the synthesis of single, non-networked, equilateral molecular triangles has been known for a long time[10,11] (see Scheme 1) and that several advances have been made in the synthesis of other polyphenylacetylene networks.[10]

Thus to conclude, this work has shown the potential of these simple polyphenylacetylene networks as molecular auxetics. We hope that given the many advantages of auxetics when compared to conventional materials, these predictions will encourage further research into their chemistry so as to enable the synthesis of the first purpose-built molecular auxetic material.

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Notes and references

† *Methods used:* (1) Simulation of the minimum energy configurations: Molecular mechanics simulations were carried out on an array of these networks (n = 1,2, …, 8) using the Cerius^2 V3.0 molecular modelling package. The polyphenylacetylene layers were aligned parallel to the Ox_2–Ox_3 planes (see Fig. 1). The energy expressions E were set up using parameters from the Dreiding force-field[12] except for the atomic charges which were calculated through the charge equilibration procedure developed by Rappé and Goddard.[13] Non-bond terms were added using the Ewald summation technique.[14] (2) Simulation of the mechanical properties:[15] The 6×6 stiffness matrix **C** (and its inverse, the compliance matrix **S**) of the minimum energy single crystalline polytriangles-*n*-yne systems were calculated from the second derivative of the potential energy function since:

$$c_{ij} = \frac{1}{V}\frac{\partial^2 E}{\partial \varepsilon_i \partial \varepsilon_j} \qquad i,j = 1,2,\ldots,6 \tag{1}$$

where E is the energy expression, V is the volume of the unit cell and ε_i are strain components. Other mechanical properties were then calculated from these matrices since, for example, the Poisson's ratios in the Ox_2–Ox_3 plane for loading in the Ox_3 direction is given by:

$$\nu_{32} = -\frac{\text{transverse strain}}{\text{axial strain}} = -\frac{\varepsilon_2}{\varepsilon_3} = -\frac{s_{32}}{s_{33}} \tag{2}$$

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