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# Design of a potentially auxetic polymer for biomedical applications

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## Calixarenes modelled on auxetic egg-rack model

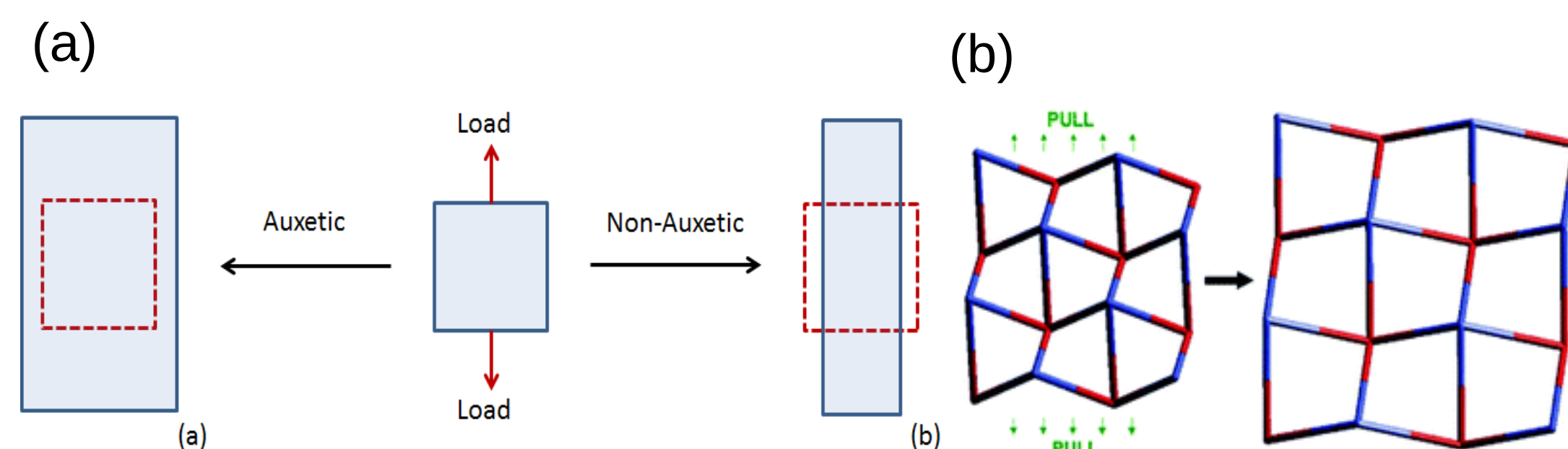


**Figure 1:** (a) The behaviour of an auxetic versus a conventional (non-auxetic) material under tension. (b) An illustration of the “egg-rack” structure and the mechanism in operation when the structure opens up under tension.<sup>1</sup>

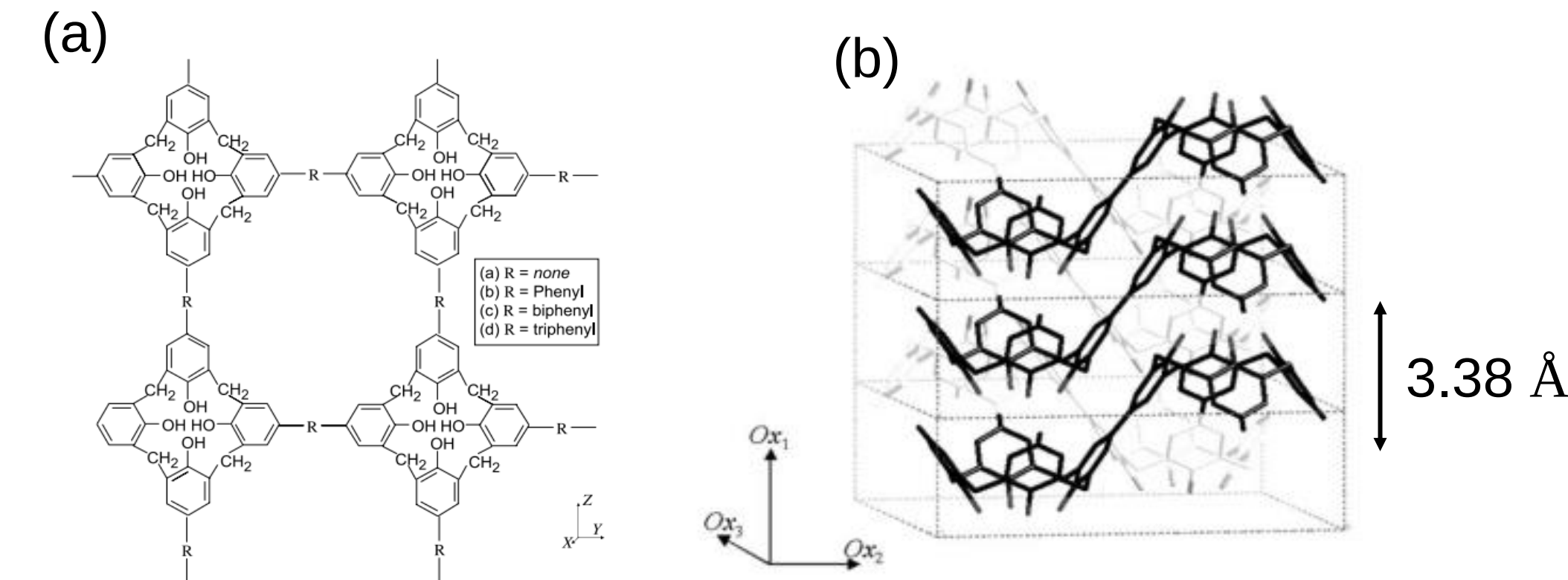


**Figure 2:** Previously modelled calixarene-based systems modelled on the egg-rack structure showing (a) the structure and (b) the minimum energy configuration of the molecular ‘double calix’ as determined using the PCFF force-field. The phenyl rings are arranged to provide optimal  $\pi$ - $\pi$  interactions with the distance between the layers, 3.38 Å being very close to that calculated for graphite (3.35 Å).<sup>1,2</sup>

## Synthetic potential

The proposed structures were deemed to be too difficult to synthesize using conventional methods, and the resulting structures would have low tensile strength in the direction where the calixarenes are only interacting through non-bond interaction. Yet, the model provides a solid foundation to build new synthetic materials which are inherently auxetic.

## Applications

- Smart filters
- More comfortable biomedical devices
- Defence and safety equipment

Tech Note

## Conclusion

A novel calixarene-based auxetic structure is proposed. This will provide a design rationale for an intrinsically auxetic calixarene-based system, leading the way towards Innovative materials with improved properties.

## Background

Auxeticity is a non-conventional property whereby a material becomes wider when stretched and thinner when compressed, a result of a negative Poisson’s ratio, a fundamental property of a material defined as the negative ratio of the transverse strain and axial strain (Fig. 1a). The design of auxetic materials is an emerging field of research, which aims to deliver new materials with improved qualities such as enhanced fracture and vibrational damping ability, augmented resistance to indentation and synclastic curvature. One geometric arrangement which has been studied and shown to be auxetic is the so-called “egg-rack” structure (Fig.1b). This consists of alternate-facing four-legged claws arranged in a square grid which open up in all directions like an umbrella when the structure is loaded in tension. A calix[4]arene-based network system has been modelled on this geometric arrangement and shown to possess auxetic properties when the calixarenes are linked through para-para biphenyl linkages (Fig. 2, Table 1).<sup>1,2</sup> In this theoretical study, we explore a different design using calix-tubes covalently linked together by phenylacetylene linkages and held into shape through supramolecular interactions within the structure (Fig. 3). We study the potential auxetic behaviour using force-field based simulations and determine the mechanical properties (Table 2).

## Novel auxetic design using Calix-tubes

**Design rationale and methodology:** A literature search on calixarene polymers was conducted to identify fragments that, when assembled in a polymer, could lead to auxetic behaviour. The selected design was constructed within the Materials Studio modelling platform. Minimisation was carried out using the PCFF force field, chosen after a validation study involving three force fields. The non-bond terms were added using the Ewald summation technique. The mechanical properties were obtained by calculating the elements of the stiffness matrix  $\mathbf{C} = [c_{ij}]$  from the second derivative of the minimised potential energy function.

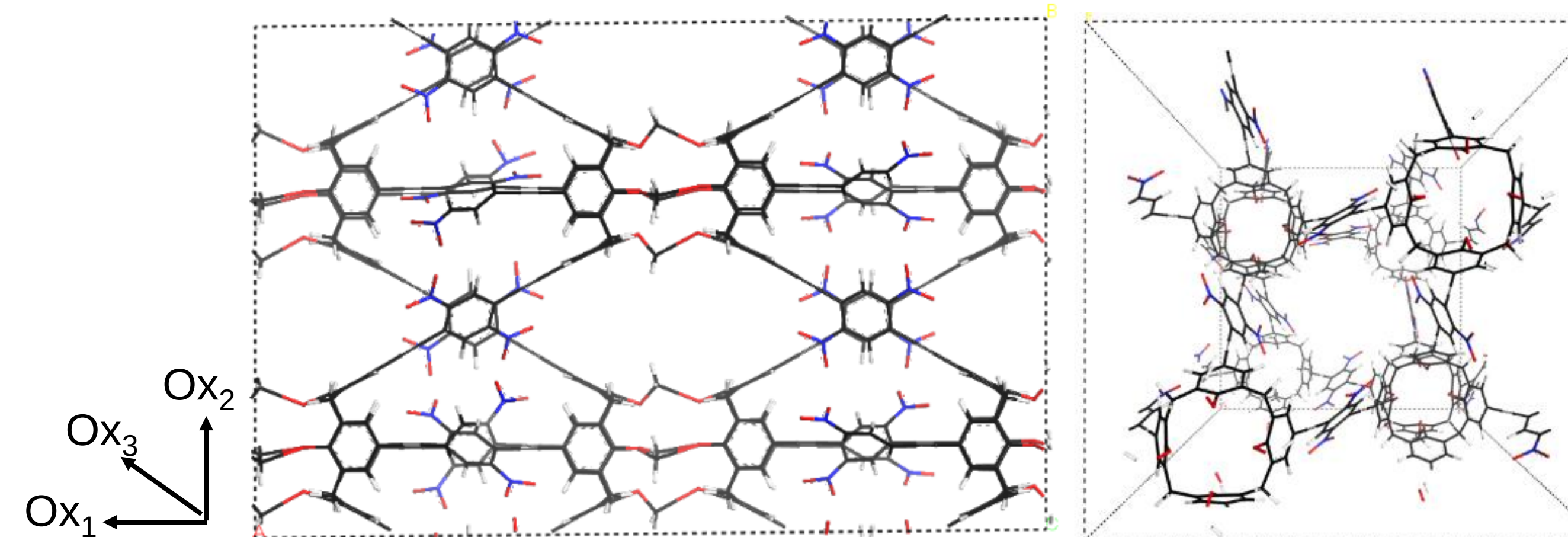


**Figure 3:** Novel design of potentially auxetic calixarenes based on Calix-tubes mimicking the “egg-rack” structure. The proposed scheme involves Calix-tubes connected by phenylacetylene linkages. Supramolecular interactions within the structure provide the necessary rigidity to keep the structure in shape and enable auxetic behaviour to be observed.

| (a)      | Egg-Rack Structure | (a): R = none | (b): R = phenyl |
|----------|--------------------|---------------|-----------------|
| $v_{12}$ | +1                 | 0.36          | 0.52            |
| $v_{21}$ | +1                 | 1.42          | 1.18            |
| $v_{13}$ | +1                 | 0.36          | 0.52            |
| $v_{31}$ | +1                 | 1.42          | 1.18            |
| $v_{23}$ | -1                 | -0.51         | -0.87           |
| $v_{32}$ | -1                 | -0.51         | -0.85           |
| $E_1$    | n/a                | 4.63          | 1.66            |
| $E_2$    | n/a                | 18.10         | 3.78            |
| $E_3$    | n/a                | 18.10         | 3.78            |

**Table 1:** (a) The simulated single-crystalline Poisson’s ratios ( $v_{ij}$ ) and Young’s moduli ( $E_i$ ) of two of the proposed molecular systems and those predicted for the idealised “egg-rack” model (i, j = 1, 2, 3). The equations defining  $v_{ij}$  and  $E_i$  are included under the table. (b) An overlay of the ‘loaded’ (grey) and the ‘unloaded’ (black) system as simulated by the PCFF force-field.<sup>1,2</sup>

(b)

$$v_{ij} = -\frac{\text{transverse strain}}{\text{axial strain}} = \frac{\epsilon_j}{\epsilon_i}$$

$$E_i = -\frac{\text{applied stress}}{\text{applied strain}} = \frac{\sigma_i}{\epsilon_i}$$

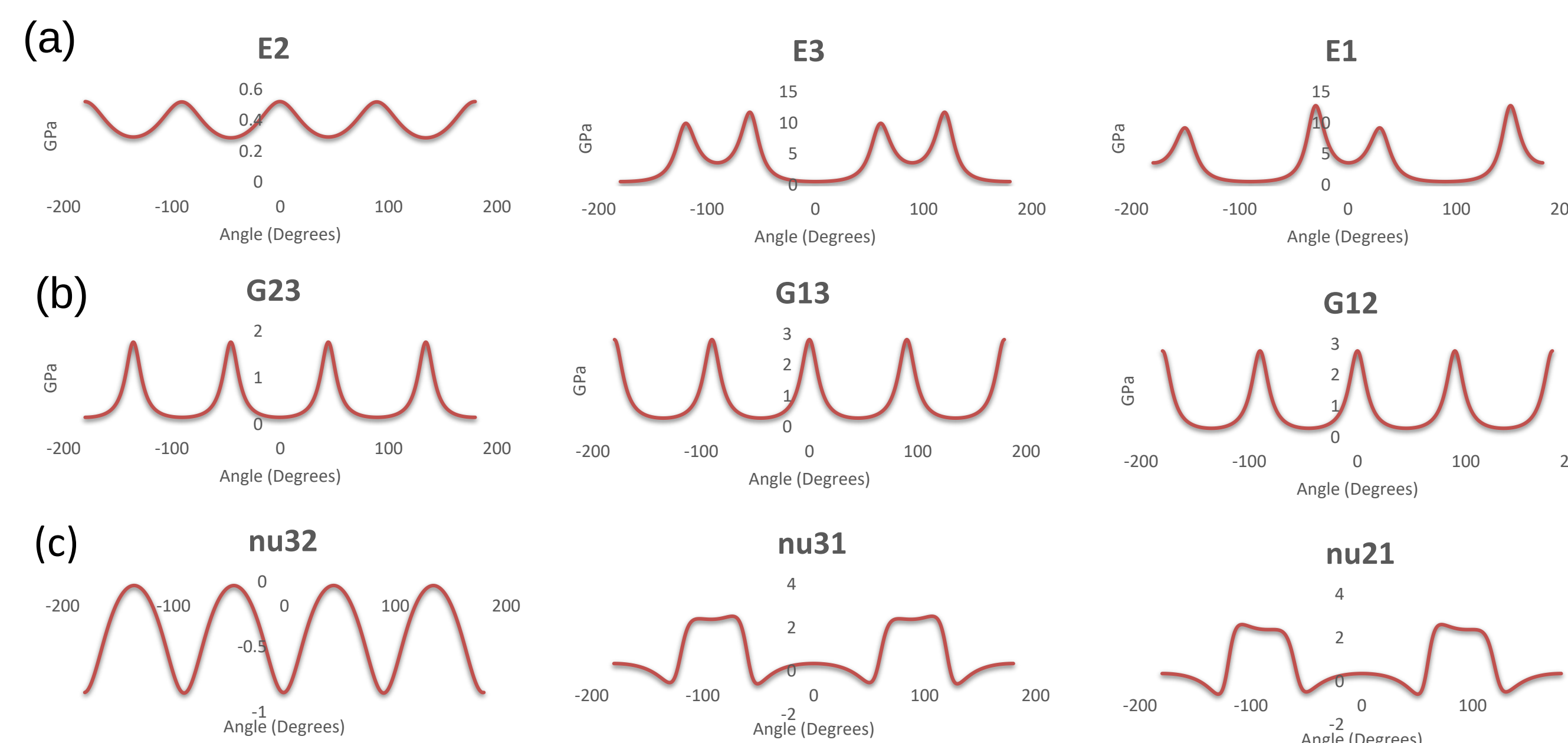


**Figure 4:** The variation of the (a) shear modulus, (b) Young’s modulus and (c) Poisson’s ratio with the angle of rotation for the proposed molecular systems. The simulated structure shows a strong negative Poisson’s ratio in the yz and zy directions, showing that it is deforming as predicted by the egg-rack mechanism. A strong positive Poisson’s ratio is obtained in the xy and xz plane.

A systematic study will be carried out to modify the structure and understand the factors which might lead to a more optimal negative Poisson’s ratio. A synthetic strategy will be devised to attempt to synthesize the optimised structure.

## References and Acknowledgements

1. J.N. Grima, J.J. Williams, K.E. Evans, *Chemical Communications*, **2005**, 4065-4067.
2. J.N. Grima, J.J. Williams, R. Gatt, K.E. Evans, *Molecular Simulation*, **2005**, 31(13), 907-913.

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