Brief Research Report

MODELLING OF CALIX(4)ARENE SYSTEMS WITH UNUSUAL MECHANICAL PROPERTIES*

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Auxetic materials exhibit the very unusual property of becoming wider when stretched and narrower when squashed [1], that is they have a negative Poisson's ratio (Fig. 1). This counter-intuitive behaviour results in many beneficial effects in the materials' properties that make auxetics superior to conventional materials in many practical applications [2]. In recent years, a number of auxetics have been manufactured by modification of the microstructure of existing materials [3], and a number of molecular level auxetics have also been proposed [1,4].

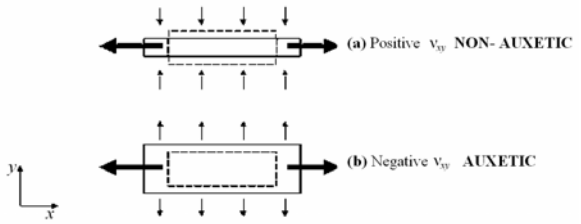

Figure 1: Illustration of conventional (non-auxetic) *vs*. auxetic behaviour.

Force-field based molecular modelling simulations have been used to investigate the potential of calix(4)arenes (Fig. 2) as building blocks for a novel class of molecular level auxetics. This newly proposed auxetic system, henceforth referred to as a calix(4)arene network (Fig. 3), offers the advantage over a number of previously proposed systems that it is made up of readily available sub-units, i.e. calix(4)arenes, the chemistry of which have been extensively investigated in recent years [5].

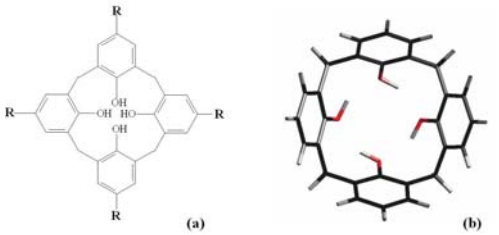

Figure 2: The structure of the simplest single calix: tetrahydroxycalix(4)arene as a) a sketch and b) constructed in the *Cerius*^{2} Graphical Interface.

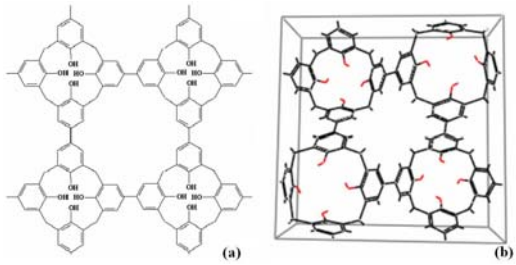

Figure 3: The unit cell of the calix(4)arene network as a) a sketch and b) constructed in the *Cerius*^{2} Graphical Interface.

In particular, an optimal methodology for the modelling and property prediction of calixarene systems was developed and validated. The development of a methodology was essential since no standard procedure is as yet available for the modelling of novel calixarene networks. The PCFF force-field within the commercially available molecular modelling software *Cerius*^{2} [6] was identified as the most suitable for the modelling of calixarene systems. The Second Derivative method [6] was found to give accurate predictions of mechanical

* *Paper presented at the Second National Chemistry Symposium, Malta, March 2004.*

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properties. The optimised methodology was then applied to a number of structural variants of the basic calixarene network. Negative Poisson's ratios, that is auxetic behaviour, was demonstrated in the majority of networks considered.

Given the many benefits of materials with negative Poisson's ratios, it is hoped that these systems would be synthesised and commercialised shortly.

References:

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[6] Molecular Simulations Inc. (MSI), San Diego, California, currently incorporated within Accelrys (http://www.accelrys.com).