Nano networks exhibiting negative linear compressibility

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Molecular mechanics simulations were used to analyse the on-axis mechanical properties of a series of nanonetworks. These consisted of naphthacene-like units linked together through acetylene chains, and designed to mimic the geometry of a winerack-like structure in one of the major planes, a geometry which is closely associated with negative linear compressibility. It was found that these networks have a potential to exhibit a negative linear compressibility in one of the major axis. Analysis of the deformation mechanism as well as the magnitudes of the compressibility in the major directions suggest that this effect arises from relative rotations of the rigid polyphenyl chains and is comparable to that predicted by an idealised winerack model deforming through hinging. This confirms that there is a very strong link between negative linear compressibility and geometry, as is the case with auxetic materials.

1 Introduction Polyphenylacetylene networks are a class of materials made from phenyl rings connected together through acetylene chains. In the last decades, these networks attracted considerable attention from the scientific community, particularly since the report by Evans et al. [1] who proposed a family of poly(phenylacetylene) networks exhibiting ‘auxetic’ behaviour, i.e. get wider when pulled rather than thinner (negative Poisson’s ratio).

From a materials design point of view, these systems are extremely versatile and can result in various 2D/3D constructs depending on how the different building blocks are connected together. In particular, Evans et al. has shown that it is possible to design 2D networks which may either be auxetic or non-auxetic, depending on the manner of substitution on the phenyl rings which could result in a re-entrant or non-re-entrant network [1–3]. More importantly, this and similar work [1–13] has suggested that a viable methodology for designing nanoscale auxetics was one which downscaled a macroscale auxetic mechanism to the atomic level, as it was shown that, provided that the material has the appropriate nanostructural features and the forms deform via the required mechanism, then auxeticity would be retained.

It is now becoming more widely recognised that auxeticity is not the only ‘negative’ mechanical property which can be explained in terms of the geometry and deformation profile of the internal structure of the material. For example, it has been shown that particular geometries and deformation mechanisms can result in the anomalous property of negative linear compressibility (NLC), i.e. the ability of a material to expand rather than contract in at least one direction when subjected to a positive hydrostatic pressure [14–38].

One of the geometries/deformation mechanisms which is known to result in NLC, is that which mimics the behaviour of a wine rack which, as a result of this geometry and constraints, can expand in one direction when being subjected to a biaxial compressive force (similar to hydrostatic pressure), i.e. exhibit NLC [27–38], see Fig. 1a. This mechanism has been used by Fortes et al. to explain NLC in methanol monohydrate [28]. These systems have provided a significant insight into the field of NLC. In particular, they have confirmed that NLC can indeed exist, and reconfirmed that a mechanism can be implemented in various classes of materials and lead to the same macroscopic properties, in this case NLC. Here it should be noted that all work carried out so far in this field has always confirmed the requirement for a positive volume compressibility unless the system is unstable [17] or the system is porous and pressure is being exerted on both from the ‘outside’ and ‘inside’. In such cases, although the system appears to expand in ‘volume’ under
positive hydrostatic pressure, the ‘solid portion’ of the system is in fact still shrinking thus not violating any thermodynamic requirement [14, 16].

From a more practical point of view, it has also been shown that negative compressibility should not be regarded as a mere scientific curiosity, as there are a number of real applications which would benefit from negative compressibility. These include the use of NLC materials in pressure sensors, artificial muscles and actuators [18, 27, 35].

Unfortunately, despite all these recent advances, it is widely recognised that this field is still in its infancy. For example, nanoscale systems exhibiting NLC which have been discovered or designed so far have limited tunability, in the sense that the nanoscale building blocks which constitute the systems permit little variability, if any. The present work will attempt to address this lacuna by proposing a novel and more tuneable polyphenylacetylene-based nanonetwork which is meant to mimic the wine rack model structure [29]. An attempt will be made to assess how slight modifications in the network’s nanostructure could result in a different set of macroscopic properties, in particular different compressibility characteristics. The behaviour of these systems at ambient pressure conditions and also at extreme negative pressure conditions are also investigated.

2 Methodology
2.1 Design concept

The concept behind this work is to design and study nanolevel systems which, as much as possible, have the nanostructural characteristics that may permit them to behave and respond to pressure in a ‘wine-rack’-like manner. This requires: (i) components which would be straight and rigid to be used as the ‘rib’ elements of the wine-rack, and (ii) components which may behave as ‘hinges’ which connect the ‘ribs’ together. These characteristics may be achieved through the use of long naphthacene-like units as the ‘rib’ elements which are connected together via acetylene chains which would act as hinges, see Fig. 1b and c. This construction is possible since the acetylene chains that are meant to act as hinges would be orthogonal to the polyphenyl naphthacene-like chain units, i.e. the different polyphenyl chains should be able to, at least in theory, rotate freely relative to each other. Through this method of design, different variants of the networks may be achieved through variation of the length of ribs by changing the number of rings between each ‘hinge’ in the polyphenyl chain and/or the length of the acetylene chains. Note that in theory, it is possible to either have ‘standard’ trellis-like systems, if the lengths of the polyphenyl linkages between the ‘hinges’ are all equal (see Fig. 1b-i), or, more complex systems where some variations are used, e.g. two different sets of lengths are used (see Fig. 1b-ii).

In the case of the system with equal polyphenyl linkages, the system may be described by a representative cuboidal unit cell (not the smallest unit cell) which, as illustrated in Fig. 1a projects as a rectangular unit cell in the plane orthogonal to the acetylene chains, i.e. plane of the ‘wine-rack’ motif. For convenience, these types of networks

![Figure 1](image-url)

Figure 1 (a) The wine-rack mechanism which results in negative linear compressibility. (b) Typical polyphenylacetylene networks consisting of polyphenyl naphthacene-like chains linked together by acetylene chains that may mimic the system in (a). The polyphenylacetylene chains can be either (b-i) equal or (b-ii) different in length. (c) The naming convention used to refer to networks where the polyphenyl chains are of equal length: \(m\) refers to the number of phenyl rings and \(n\) refers to the number of acetylene linkages, hence the name \(PmAn\).
are henceforth referred to as PmAn networks, where ‘m’ refers to the number of phenyl rings denoted by ‘P’ and ‘n’ refers to the number of acetylene links denoted by ‘A’. This wine-rack motif displayed by such systems, see Fig. 1, has been extensively modelled and it was shown that for a system with unit thickness in the third direction, the compressibility properties, if deformations are limited to changes in \( \theta \) (the angle between the ribs in the ‘wine-rack’) should be estimated by [29]:

\[
\beta^b_x = -\frac{1}{k_h} \cos(\theta) \tan \left( \frac{\theta}{2} \right),
\]

\[
\beta^b_y = \frac{1}{k_h} \cos(\theta) \cot \left( \frac{\theta}{2} \right),
\]

where \( \beta^b_x \) and \( \beta^b_y \) are the linear compressibilities in the x- and y- directions respectively, assuming that the wine-rack deforms only through hinging, and \( k_h \) is the hinging stiffness constant. These equations suggest that these systems are capable of exhibiting negative compressibility properties, in particular, negative \( \beta_x \) for \( 0^\circ < \theta < 90^\circ \) and a negative \( \beta_y \) for \( 90^\circ < \theta < 180^\circ \). Moreover, they suggest that the ratio of the compressibility ratios should be:

\[
\frac{\beta^b_y}{\beta^b_x} = -\cot^2 \left( \frac{\theta}{2} \right).
\]

Obviously, this idealised uni-mode behaviour is difficult to achieve in real systems. This makes it necessary to perform more detailed simulations so as to estimate better the true properties that could be achievable by such systems.

### 2.2 Simulations

#### 2.2.1 Construction of the system

Simulations were performed on six variants of the polyphenylacetylene networks of the simpler ‘standard’ system shown in Fig. 1b, where \( m = 1, 2 \) and \( n = 1, 2, 3 \). These systems were constructed within Materials Studio (version 7.0) as molecular crystals through the use of periodic boundary conditions. The networks were oriented in such a way that the acetylene chains are aligned parallel to the c crystal axis, while the polyphenyl chains are aligned along the diagonals of the crystal plane orthogonal to the acetylene chains. This method of construction results in a unit cell which, if the system has a geometry where the acetylene and polyphenyl chains are perfectly straight, the cell parameters \( a, b \) and \( y \) would be all equal to \( 90^\circ \). The crystal lattice itself was aligned with the global x-, y- and z-directions in such a way that the c crystal axis is always parallel to the global z-direction, the b crystal axis lies in the yz-plane whilst the a crystal axis is free to orient itself in any direction. With this orientation, the \( a, b, c \) lattice vectors would be in the form:

\[
a = (a_x \quad a_y \quad a_z),
b = (0 \quad b_y \quad b_z),
c = (0 \quad 0 \quad c_z),
\]

where \( a_x, b_y \) and \( c_z \) are the projected lengths of the unit cell in the x-, y- and z-directions, respectively (hereafter referred to as X, Y and Z, respectively) and may be expressed in terms of the cell parameters as follows:

\[
a_x = \sqrt{a^2 - (a\cos(\beta))^2 - \left( \frac{abc\cos(\gamma) - ab\cos(\alpha)\cos(\beta)}{b\sin(\gamma)} \right)^2},
\]

\[
b_y = bsin\alpha,
\]

\[
c_z = c,
\]

where \( a, b \) and \( c \) are the lengths of the lattice vectors \( a, b \) and \( c \), respectively whilst \( \alpha, \beta \) and \( \gamma \) are the angles between the lattice vectors ‘b’ and ‘c’ ,‘a’ and ‘c’ and ‘a’ and ‘b’ , respectively.

It should be emphasised that the systems so constructed are not the smallest possible representations of these molecular crystals. In fact, an even smaller rhombic unit cell could have been chosen with the polyphenyl chains being placed parallel to the crystallographic axis \( a \) and \( b \). It should also be noted that throughout this work, all simulations were always performed on a \( 2 \times 2 \times 2 \) super lattice of the smallest rectangular unit cell. This unit cell size was found to be large enough to adequately represent the expected true properties of the system. In fact, even simulations performed on the smaller \( 1 \times 1 \times 1 \) rectangular unit cells were found to give comparable results and, therefore, even the smaller unit cell could, in theory, have been used. No symmetry constraints were applied, i.e. a P1 symmetry was used.

#### 2.2.2 Simulations

For each of the systems constructed, the energy expression was set up using the Dreiding force-field [39] as implemented in the Forcite module within Materials Studio. The default settings were used with the exception of the summation method of the non-bond interactions, which were summed up using the Ewald summation technique [40]. Atomic charges were calculated as point charges using the charge equilibration procedure as developed by Rappe et al. [41]. This force-field has been used in earlier studies to study other polyphenylacetylene systems, in particular their mechanical properties and auxetic potential [2–4]. Once the energy expression was set up, the potential energy of the structure was then minimised as a function of the atomic coordinates and six cell parameters at an external pressure \( p = 0.00 \text{ GPa} \) using a compound minimiser (the SMART minimiser as implemented in Materials Studio Forcite) which starts off
with the steepest descent algorithm and then proceeds with other more efficient Adopted Basis Newton-Raphson method, and quasi-Newton methods. Minimization was considered as complete when the RMS gradient was less than 0.04 kcal mol\(^{-1}\) A\(^{-1}\).

The elastic constants of the systems were then simulated through a constant-strain approach using the Forcite module within Materials Studio which computes the \(6 \times 6\) compliance matrix \(\mathbf{S}\) relating an applied stress \(\mathbf{\sigma}\) to the resultant strain \(\mathbf{\epsilon}\). For these simulations, four distorted structures were generated for each strain pattern and the maximum strain amplitude was set to 0.003, i.e. 0.3% strain. This low value of maximum applied strain was used so as to ensure that the stress–strain behaviour remains as much as possible approximated by a linear relationship. From this computed compliance matrix, the on-axis linear compressibility coefficients \(\beta_x\), \(\beta_y\), and \(\beta_z\) in the \(x\)-, \(y\)-, and \(z\)-directions, as well as the area compressibility \(\beta_A\) in the \(xy\)-plane and the volume compressibility \(\beta_V\) were calculated as follows:

\[
\beta_x = -\frac{1}{X} \left( \frac{\partial \mathbf{X}}{\partial p} \right)_T = -\frac{1}{a_x} \left( \frac{\partial a_x}{\partial p} \right)_T = s_{11} + s_{12} + s_{13},
\]

\[
\beta_y = -\frac{1}{Y} \left( \frac{\partial \mathbf{Y}}{\partial p} \right)_T = -\frac{1}{b_y} \left( \frac{\partial b_y}{\partial p} \right)_T = s_{21} + s_{22} + s_{23},
\]

\[
\beta_z = -\frac{1}{Z} \left( \frac{\partial \mathbf{Z}}{\partial p} \right)_T = -\frac{1}{c_z} \left( \frac{\partial c_z}{\partial p} \right)_T = s_{31} + s_{32} + s_{33},
\]

\[
\beta_A = \frac{1}{XY} \left( \frac{\partial \mathbf{X} \mathbf{Y}}{\partial p} \right)_T = \frac{1}{a_x b_y} \left( \frac{\partial a_x b_y}{\partial p} \right)_T = s_{11} + s_{22} + 2s_{12} + s_{13} + s_{23},
\]

\[
\beta_V = \frac{1}{XYZ} \left( \frac{\partial \mathbf{X} \mathbf{Y} \mathbf{Z}}{\partial p} \right)_T = \frac{1}{a_x b_y c_z} \left( \frac{\partial a_x b_y c_z}{\partial p} \right)_T = s_{11} + s_{22} + s_{33} + 2s_{12} + 2s_{13} + 2s_{23},
\]

where \(E_x\) and \(E_y\) are the Young’s moduli in the \(x\)- and \(y\)-directions respectively, \(G_{xy}\) is the shear modulus in the \(xy\)-plane whilst \(v_{xy}\) and \(v_{yx}\) are the Poisson’s ratio in the \(xy\)-plane for loading in the \(x\)- and \(y\)-directions, respectively.

Furthermore, in an attempt to understand better the effect of pressure on the crystal structure and compressibility properties of these systems, in particular their potential to exhibit NLC, the systems so obtained were then re-minimised at various values of externally hydrostatically applied pressure to a maximum of 0.50 GPa in increments of 0.05 GPa. Also, the system at 0.00 GPa was then re-minimised at negative pressures to a minimum of \(-0.50\) GPa in increments of \(-0.05\) GPa, then to a minimum of \(-3.00\) GPa in increments of \(-0.25\) GPa and then to a minimum of \(-5.00\) GPa in increments of \(-0.50\) GPa.

Finally, in attempt to confirm that the results obtained by the Dreiding force-field were not an artefact of the force-field used, additional simulations were also performed on these systems using other potentials. In particular, the simulations were repeated using COMPASS and Universal force-fields using their default settings with the exception of the summation method for non-bond interactions which were once again summed up using the Ewald summation technique. For simulations using COMPASS force-field, the atomic charges were calculated using force-field assigned values whilst with the Universal force-field (UFF), the charges were calculated using the charge equilibration by Rappé et al. [41].

### 3 Results and discussion

All the simulations were carried out successfully in the sense that all systems reached the set convergence criteria. Images of the \(xy\)-plane projected cross-sections of a typical \(Pm\text{An}\) system at different hydrostatic pressures, as simulated by the Dreiding force-field, are shown in Fig. 2 whilst plots of \(X, Y\) and \(Z\) the projections of the systems in the \(x\)-, \(y\)- and \(z\)-directions are shown in Fig. 3. (The equivalent plots for the projections as obtained by the other force-fields are shown in the supplementary information.)

These images suggest that for all systems, the networks project in the \(xy\)-plane as a wine-rack like geometry where, at near ambient hydrostatic pressures, the ‘wine-rack’ is semi-closed whilst at high negative pressure, the ‘wine-rack’ appears to be fully-open. This indicates that there is a significant shrinkage in the \(y\)-direction relative to the system at 0.00 GPa as the system opens up under the conditions of high negative pressure. Although \textit{a prima facie} these structural changes are indicative of a giant negative linear compressibility, the term can only be loosely applied since the changes in the linear dimensions occur very suddenly as evident from Fig. 3, suggesting that this ‘giant negative linear compressibility’ is in fact resulting from a phase change. Large changes in linear dimensions associated with pressure-induced phase transitions are not unusual and have also been observed in naturally occurring crystals. In this particular case, it is worth noting that the changes in dimensions, i.e. the contraction in the \(y\)-direction...
accompanied by a sudden expansion in the $x$-direction, result in an overall increase in area (in the $xy$-plane) and volume (see Fig. 4) at negative pressures, and is in line with what is expected to happen when a system undergoes a ‘wine-rack’-like deformation (see Fig. 4).

Here it must be noted that it is also evident that at near ambient pressures, the attractive $\pi-\pi$ interactions [42] dominate and result in a conformation where the polyphenyl chains tend to stack in a manner which optimizes these interactions, thus explaining why at such pressures the networks mimic a ‘semi-closed wine-rack’. In fact, with no externally applied pressures, the inter-phenyl layer separation $d$ (see Fig. 1a) as simulated by the Dreiding force-field was approx. $3.45 \pm 0.03$ Å (see Supporting Information for variation of the inter-phenyl layer separation with pressure), a separation which is suggestive of $\pi-\pi$ stacking and comparable to that in graphite, $3.35$ Å [43]. Also, at low pressures, both positive and negative, such stacking was preserved. In particular, the inter-phenyl separation in the case of the Dreiding force-field ranged from ca. $3.39 \pm 0.02$ Å at $p = 0.50$ GPa to $3.51 \pm 0.04$ Å at $p = -0.50$ GPa. Although these changes are non-negligible, they are insignificant when compared to the changes observed at higher values of negative pressure, when the networks are in their fully open conformation. More specifically, the inter-phenyl separation for the $P1An$ systems was ca. $5.03 \pm 0.01$ Å at

**Figure 2** Projections in the $xy$-plane of the $P1A1$ network simulated using the Dreiding force-field [39] at (i) $-5.00$ GPa, (ii) $-2.00$ GPa, (iii) $-0.50$ GPa, (iv) $0.00$ GPa and (v) $+0.50$ GPa (see also animations, Supporting Information).

**Figure 3** Variation of the (a) $X$, (b) $Y$ and (c) $Z$ projections with pressure in the range $-5$ GPa $\leq p \leq +0.5$ GPa for the various $PmAn$ modelled using the Dreiding force-field.

**Figure 4** Variation of the (a) area and (b) volume with pressure in the range $-5$ GPa $\leq p \leq +0.5$ GPa for the various $PmAn$ modelled with the Dreiding force-field.
−2.00 GPa, a pressure at which the systems had already opened up but not yet in their fully open form, whilst that of P2A\textit{n} systems was 7.56 ± 0.03 Å. These separations continue to increase slightly further to ca. 5.11 ± 0.04 Å for the P1A\textit{n} systems and 7.74 ± 0.09 Å for the P2A\textit{n} systems at −5.00 GPa. At this point, the systems are virtually fully opened. Beyond this point, the negative compressibility would not be observed and instead the system behaves in a conventional manner \textit{vis-à-vis} its compressibility. This can be confirmed by the negative slopes in plots of the dimension of the unit cell vs. pressure. In fact, the abrupt changes in the cell projections that are occurring at negative pressures, and which indicate a pressure-induced phase change, are in line with the behaviour in inter-phenyl separation. This behaviour is indeed to be expected since, as the extent of negative pressure increases, the forces being applied on the system will eventually be greater than those holding the different layers together resulting in sudden opening of the system.

It is also interesting to note that the negative pressure at which the phase change occurred was different for each of the systems modelled, where for the P1A\textit{n} series, the pressure required to open up P1A3 was lower than that required by the P1A2, which in turn was lower than that required by the P1A1. This behaviour was also observed for the P2A\textit{n} series. This may be explained by the fact that upon increasing the length of the acetylene chain, the density of the systems decreases, as does the density of the \(\pi-\pi\) interactions, thus permitting opening of the system at a less negative value of the hydrostatic pressure.

Furthermore, it should be highlighted that systems within each of the series considered (P1A\textit{n} and P2A\textit{n}), deformed in a similar manner, where it seems that the length of the acetylene chain does not markedly affect the extent of deformation but only the pressure at which the phase change occurs. This is in sharp contrast to what was observed when comparing systems from the two different series but with the same \(n\)-value. As evident from Fig. 3, the phase change resulted in very different extent of expansions in the \(x\)-directions, with almost doubling in size for the P1A\textit{n} systems and a tripling in size for the P2A\textit{n} systems. In fact, comparing the systems at −2.00 GPa to those at 0 GPa, a (93 ± 1)% increase in the \(x\)-projection was observed for the P1A\textit{n} systems and a (199 ± 1)% increase for the P2A\textit{n} systems. Once again, this type of behaviour was to be expected since, as the extent of negative pressure increases, the forces being applied on the system will eventually be greater than those holding the different layers together resulting in sudden opening of the system.

As evident from Fig. 1a, for a given angle \(\theta\), the \(x\)-projection of the ‘wine-rack’ geometry is given by \(X = 2\cos(\frac{\theta}{2})\) so that one would have expected a \(\frac{dX}{d\theta}\) of ca. 92% as \(\theta\) changes from 136.74° at 0 GPa to 90° at −2.00 GPa in the case of the P1A\textit{n} systems and ca. 194% as \(\theta\) changes from 152.19° at 0.00 GPa to 90° at 0.00 GPa in the case of the P2A\textit{n} systems. These values are well within the range of what was really observed, i.e. a (93 ± 1)% for the P1A\textit{n} systems and (199 ± 1)% for the P2A\textit{n} systems. Similar arguments can also be made for the contractions observed in the \(y\)-projections where, based on the angles measured in the molecular networks, the analytical models [29] predicted a shrinkage of 24 and 27% whereas the simulations with the Dreading force-field suggested a giant negative linear compressibility resulting in shrinkage of (23 ± 0) and (26 ± 0)% for the P1A\textit{n} and the P2A\textit{n} systems, respectively when comparing the systems at −2.00 GPa to those at 0.00 GPa. Similar overall trends, for example, giant contractions and expansions in the \(x\)- and \(y\)-directions, respectively, upon applications of negative pressure, were obtained by UFF and Compass force-fields thus confirming that these results are not artefacts of the potential used (see Supplementary Information).

All this is very significant as it suggests that by varying the length of the acetylene chain and/or the number of phenyl rings, one may alter and fine-tune the macroscopic properties of the system, including the pressure at which the system undergoes the phase change, and the extent of changes in the linear dimensions resulting through the phase-change, thus providing a blueprint for producing materials with tailor-made properties. More importantly, the giant change in dimensions that have been predicted to take place once the applied pressure is large enough to overcome the \(\pi-\pi\) interactions holding the system together, suggests that systems such as these can find applications for the design of pressure sensors. In this respect, it should be noted that these sudden changes in dimensions are likely to be accompanied by other changes in the macroscopic properties, e.g. the conductivity properties.

The behaviour of the systems at near ambient conditions is also interesting. In fact, on closer inspection, it becomes clear that when low pressures are being applied, the P1A\textit{n} systems behaved rather differently from the P2A\textit{n} systems, with the P1A\textit{n} systems exhibiting much more pronounced negative compressibility properties in the \(y\)-direction, as illustrated in Fig. 5. This enhanced NLC of P1A\textit{n} compared to P2A\textit{n} may be explained, at least partially, through geometric arguments. In fact, the P1A\textit{n} systems project in the \(xy\)-plane with a ‘wine-rack’ like geometry where the angle \(\theta = 136.74° \pm 0.08°\), giving idealised compressibility values of \(\beta_x = \frac{1}{\lambda_x} 1.84\) and \(\beta_y = -\frac{1}{\lambda_y} 0.29\), i.e. \(\frac{\beta_y}{\beta_x} = -0.16\) whilst the P2A\textit{n} have a geometry where \(\theta = 152.19° \pm 0.04°\) resulting in lower idealised compressibility values of \(\beta_x = \frac{1}{\lambda_x} 3.57\) and \(\beta_y = -\frac{1}{\lambda_y} 0.22\), i.e. \(\frac{\beta_y}{\beta_x} = -0.06\). In other words, the idealised model by Grima et al. [29] is suggesting that from a geometry point of view, the P1A\textit{n} should exhibit more enhanced negative compressibility properties than the P2A\textit{n} systems, something which was indeed also observed in the simulations (see Table 1 which lists the simulated mechanical properties at \(p = 0.00\) GPa obtained though the constant strain method with small
strains of up to 0.3% being applied). However, the simulations also suggest some additional reduction in the extent of negative compressibility and whilst the P1An and P2A1 systems all exhibited a negative \( \beta_x \), negative compressibility in the \( y \)-direction as \( p \rightarrow 0.00 \) GPa for the P2A2 and P2A3 systems could not be confirmed. In fact, the simulations on the P2A2 and P2A3 carried out at different pressures with different force-fields predicted different and more complex trends (see Fig 5) with the behaviour under positive hydrostatic pressure sometimes following a different trend than that observed at negative pressures. This may be due to the fact that the systems with longer polyphenyl chains would have more pronounced \( \pi-\pi \) interactions thus forcing these nanosystems to behave in a manner which is less dictated by the geometry of sub-units.

In view of the more pronounced negative compressibility exhibited by the P1An systems, the discussion will now focus on these systems. For these systems, it was found that when the P1An systems where subjected to pressures in the range \(-0.50 \) GPa \( \leq p \leq +0.50 \) GPa, the systems deform in such a way that the polyphenyl chains hinge about the acetylene linkages, so that the whole structure behaves once again as a nanolevel ‘wine-rack’-like structure. In fact, as illustrated in Fig. 6a, there are changes of \( c \cdot 2^\circ \) in the angle \( \theta \) between the polyphenyl chains as projected in the \( xy \)-plane, which changes are accompanied by less significant changes in length \( l \) (see Fig. 6b), of the polyphenyl chains themselves, thus confirming a ‘wine-rack’-type behaviour. As evident from Table 1, there is an overall good agreement between the behaviour of these nanonetworks as simulated by the Dreiding force-fields and the much simpler analytical model based on geometry [29]. Particularly remarkable is the fact that the magnitude of the compressibility also exhibit similar ratios. It is also interesting to note that in all cases, the Young’s moduli in the \( x \)-direction are much lower than the Young’s moduli in the \( y \)-direction, this being in accordance with the wine-rack model presented elsewhere [44] as a possible model for non-auxetic foams, although this idealised hinging model had predicted higher values for the positive Poisson’s ratio for stretching in the \( y \)-direction, meaning that the deviations from the idealised hinging ‘wine-rack’ model could be resulting from this deviation. This may be explained by the fact that, had the idealised behaviour been observed, stretching in the \( y \)-direction, would have resulted in an excessive shrinkage in the \( x \)-direction, and \textit{ipso facto}, a reduction in the inter-layer separation, something which would have been opposed by the non-insignificant repulsive part of non-bond interactions.

All this is very significant as it gives a clear confirmation that, in analogy with earlier work on designed materials with a negative Poisson’s ratio [1–13, 45–49], it should be possible to design materials that exhibit negative linear compressibility by ensuring that the nanostructure of

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**Figure 5** Variation in strains along the (a) \( x \), (b) \( y \) and (c) \( z \) directions at low pressure values of \(-0.50 \) GPa \( \leq p \leq +0.50 \) GPa for the PmAn systems modelled with the Dreiding force-field.

**Table 1** Mechanical properties for the various PmAn polyphenylacetylene networks simulated by the Dreiding force-field at pressures close to 0.00 GPa.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Young’s moduli (GPa)</th>
<th>Poisson’s ratio</th>
<th>compressibility (TPa⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E_x )</td>
<td>( E_y )</td>
<td>( \nu_{xy} )</td>
<td>( \nu_{yz} )</td>
</tr>
<tr>
<td>P1A1</td>
<td>28.6</td>
<td>380.6</td>
<td>0.16</td>
</tr>
<tr>
<td>P1A2</td>
<td>24.3</td>
<td>295.1</td>
<td>0.16</td>
</tr>
<tr>
<td>P1A3</td>
<td>21.6</td>
<td>242.1</td>
<td>0.16</td>
</tr>
<tr>
<td>P2A1</td>
<td>30.5</td>
<td>604.0</td>
<td>0.06</td>
</tr>
<tr>
<td>P2A2</td>
<td>25.4</td>
<td>450.4</td>
<td>0.06</td>
</tr>
<tr>
<td>P2A3</td>
<td>19.0</td>
<td>305.5</td>
<td>0.02</td>
</tr>
</tbody>
</table>
the material has the necessary geometrical features that enable it to mimic known mechanisms that can achieve this effect.

Before concluding, it should be emphasised that the work presented here was based entirely on simulations, and a definite proof whether NLC is indeed exhibited by such systems will only be available once such materials are manufactured and tested. The behaviour of such real materials may differ to some extent from what is predicted here, since in this work we only considered defect free materials, a level of perfection which may be difficult to achieve in practice. More importantly, it may be necessary to modify the systems proposed to facilitate synthesis. Any such modification is likely to have some effect on the macroscopic properties of the systems and further investigations may need to be done to recalculate the predicted compressibility properties. Nevertheless, given the excellent agreement between the analytical model and the properties predicted here, it is more than likely that these, or related, materials which are meant to mimic the ‘wine-rack’ model would indeed exhibit NLC to some extent or another.

4 Conclusions This work has shown that it is should be possible to design polyphenylacetylene-based materials which may exhibit the anomalous property of negative linear compressibility by mimicking the wine-rack model. It was shown that such materials are likely to be stable as they do not violate the requirement that the volume compressibility is positive. These materials may also have some of their macroscopic properties fine-tuned through changes in their design.

Supporting Information Additional supporting information may be found in the online version of this article at the publisher’s web-site.

References