

*Dedicated to Professor Alexandru T. Balaban
on the occasion of his 85th anniversary*

SUPER-MOLECULES

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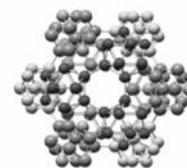
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The idea of “super-molecules” comprised from a given set of common molecular building blocks is addressed. Some examples are illustrated, and some interesting related issues are raised – including the emergence of a characteristic set of low-frequency vibrations, and the possibility of super-structurally shielded polyradicaloid spins.



INTRODUCTION

The term “super-molecule” should perhaps be clarified a bit. Here we mean by this that an overall structure (or better “super-structure”) is constructed from a collection of molecular building units – such as a buckyball, or other fullerene, or a carborane unit, or an adamantane unit, or a benzene unit. The distinction from a “polymer” is that the overall super-structure has a deliberate, perhaps elaborate, characterization in terms of something much like a molecular structure. Polymers have an overall such structure, which is nearly always viewed as that of a simple linear chain. The “super-structure” or “super-molecules” is that of another molecule, shape or polyhedron such as a larger carborane. Often the polymer might even be viewed as any of different chains of different (long) lengths – whereas our “super-molecules” most typically have a precise number

of building units stuck together in a very particular structure. Admittedly, many biological polymers such as proteins and nucleic acids have well-defined short- and long-range order of the units, but the “super-structure” is that of simple chain -- rather like that of elemental selenium, -Se-Se-Se-... Indeed polymers of a (small) fixed number of polymer units are often distinguished as “oligomers”, though the number of units in an oligomer is typically viewed to be easily variable, whereas the super-molecules considered here rather often have the number of building units dictated by the overall super-structure. Here the super-structure is often that of a polyhedron. In any event the distinction between polymers, oligomers, & super-molecules is somewhat a matter of degree – *i.e.*, it is a somewhat subjective designation. The noun “super-molecule” should also be distinguished from the adjective “supramolecular” for which the latter a small

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number of highly functionalized molecules which are strongly, but generally not covalently, coupled, such as is found in catenanes and rotaxanes.

As an example of a super-molecule structure, we might note the “super-carborane” molecule with an overall super-structure of an icosahedron, comprised from 12 component carboranes arranged at the corners of this super-icosahedron. This is illustrated in Fig. 1, when the component carborane units p - $C_2B_{10}H_{12}$ (*i.e.*, 1,12- $C_2B_{10}H_{12}$) each with 5 H-atoms removed (from the 5 B-atoms around one of the C-atoms) are each bonded to their 5 neighboring carborane units, so as to preserve the bonding pattern around each atom. Indeed this super-molecule is already considered¹ (along with the possibility of a super-super-carborane). Of course, very many other super-structures and very many other building units are possible.

The present idea of “super-molecules” assimilates naturally into the wide-spread ideas of nano-structures and nano-technology – but perhaps with a greater emphasis on classical chemical ideas, just shifted from molecular structures to molecular super-structures. Indeed carboranes as potential versatile building units for nano-structures have been emphasized repeatedly^{2,4} -- where the “versatility” has to do with the different multiplicity (*i.e.*, 12 in the current case) of inter-unit connections in a variety of directions – *i.e.*, they were viewed as a versatile molecular “tinker-toy” unit. But again very many building units may be imagined.

Such ideas would naturally be anticipated to be of general chemical interest – *e.g.*, to a general chemical researcher such as A. T. Balaban to whom this paper is dedicated. Indeed a foresightful indication of this super-molecule idea can be identified in Sandy Balaban’s⁵⁻⁸ idea for the nomenclature of general polymantanes. There the

building units are each adamantane unit, and the super-structure is correlated with positions at the centers of the adamantane units, with connections between such positions made whenever the corresponding adamantane cells are “fused” by sharing a 6-membered ring. This is shown in Fig. 2 for a tetramantane, where the super-structure of central positions looks like the carbon skeleton of one of the conformations of n -butane. Indeed rather generally these polymantane super-structures (of which now many are experimentally known⁹⁻¹¹) look like different saturated hydrocarbon conformations – with the many now experimentally known cases involving such a super-structure often corresponding to an unbranched saturated hydrocarbon conformations, namely those of an alkane. Sandy Balaban then proposed a nomenclature for the polymantanes which is expressed in terms of the corresponding super-structural alkane conformations. There is of course a problem with this when the super-structural saturated-hydrocarbon conformations start becoming cyclic or multi-cyclic, and so include the polymantanes which are the species being sought to be named – though Sandy¹² as well as others¹³ have considered this (formalistically) elsewhere.

Moreover, (aside from nomenclatural issues) Sandy Balaban has gone ahead to consider¹⁴ polymeric super-structures for his polymantanes, evidently as components of nano-structures such as proposed by Drexler¹⁵ and others¹⁶⁻¹⁸ to make different nano-machines, and other nano-devices. The general idea seems to be to identify possibilities for singularly strong (*e.g.* nano-diamondoid) structures. In Sandy’s recent work¹⁴ some effort is directed to trying to elucidate the stresses which might arise in such structures as might be imagined to be appropriate for molecular machines.

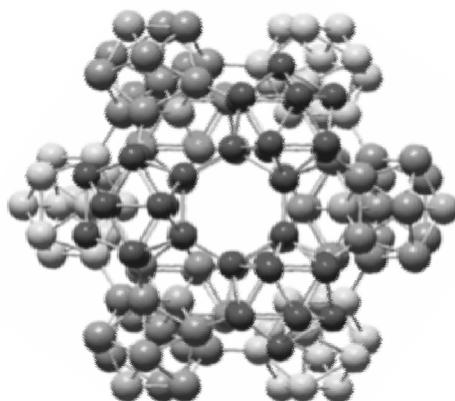
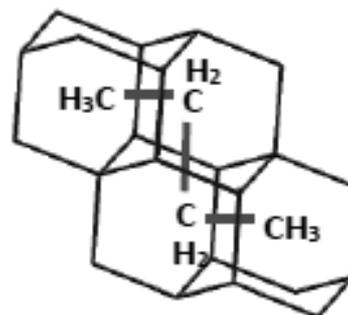


Fig. 1 – Super-carborane with H atoms not shown. Nearest vertices colored red, followed by rainbow colors (orange, yellow, and green) as the distance from the observer increases.

Fig. 2 – The Tetramantane C-skeleton corresponding to the totally staggered or anti-conformation of *n*-butane, as is shown inside Tetramantane.



In connection with the idea of super-molecules one naturally wonders not only about the possibilities, but also whether there might be any “emergent” characteristics of the super-molecular structures. Here we try to indicate something about the possibilities -- and some different emergent features, *e.g.*, relating to stress and strain, or to super-structural vibrational modes.

ADAMANTANE-BASED SUPER-STRUCTURES and BEYOND

The building units in polymantanes lack the features of many polymer structures, in that the monomer units are fused together at faces. That is, though fusion of adamantane units at faces is conceivable mathematically, this fusion does not correspond to a chemical process. In typical polymerization process the monomer skeleton remains intact with ligand units being deleted to allow formation of new bonds between monomer units. And moreover most polymerizations involve formation of just a single bond between monomer units, whereas in polymantanes multiple interconnections are formed. That the polymantanes arise naturally in certain naturally occurring natural gas sources still indicates a chemically reasonable process for their synthesis. And yet also the most extended of polymantanes (namely diamond) has long been known in nature – and experimentally prepared.¹⁹⁻²¹

Indications of some of the complications involved are indicated in understanding the gross chemical formulas for different sorts of polymantanes. Gross chemical formula for adamantane is $C_{10}H_{14}$ and that for an *n*-unit linear-chain polymantane may be viewed to be times that for adamantane minus *n*-1 times that (C_6H_{12}) for each of the face-fusions – thus $C_{4n+6}H_{2n+12}$. And this persists for those (so-called *cata*-condensed) polymantanes corresponding to branched alkanes

of *n* carbons. Indeed polymantanes corresponding to a more general number of face-fusions, one just need subtract other appropriate numbers of C and H atoms, depending on the mode of fusion, *e.g.*, whether it is a *peri*-fusion of the completion of a cycle. But there is a remaining problem if adamantane cells instead of sharing a face (of 6 carbons) only share a single C—C edge or a single C-atom, whence one needs to also count up the number of such contacts – subtracting appropriate numbers of C and H atoms for each sharing of a single C—C edge or each sharing of a single C-atom. With the allowance of these additional sorts of contacts between adamantane cells, one also perceives complications with the earlier indicated nomenclatural ideas.

As to polymers of a more traditional kind one might simply consider interconnection between adamantane units by a single C—C bond external to the cells, rather than via a face (or edge or atom) fusion. Thus for instance, one might entertain an adamantane super-structure made from component units of tetrahedral symmetry, such as adamantane itself – the interconnections being at the sites which would be tertiary in the adamantanes before interconnection. (Interconnections are also conceivable²² at the component adamantanes, but the current choice is more natural for a component with tetrahedral symmetry – and tetrahedral angles between the “external” bonds.) The resultant super-adamantane²³ is illustrated in Fig. 3. And one might naturally iterate this process to make super-super-adamantane – or higher toward a fractal. Yet further one might entertain many different tetrahedral symmetry structures, with an associated quartet of externally radiating bonds to be a sort of super-carbon atom to construct a great variety of super-structures corresponding to any classical saturated hydrocarbon. Indeed an effort has been made²⁴ to identify a vast host of such super-carbon atoms.

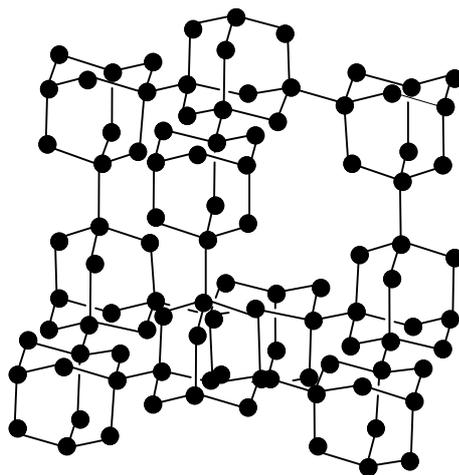


Fig. 3 – Super-adamantane (with H atoms omitted).

STRESSES, ANGLE-STRAIN, AND SUPER-STRUCTURAL VIBRATION

Sometimes there are energy costs, which are not so readily ascribed to strained bond angles or strained bond lengths. We note, for example, that the measured enthalpies of formation²⁵ per C atom of cyclohexane, adamantane, and diamantane proceed comfortably linearly as befits their descriptions as $(\text{CH}_2)_6$, $(\text{CH})_4(\text{CH}_2)_6$, $(\text{CH})_8(\text{CH}_2)_8$. This linearity may be conveniently interpreted as being due to different proportions of H atoms, and of corresponding different proportions of C atoms of secondary (or tertiary) functionality (where the local electron wave-function around such C atoms must be slightly different. Though one might speak of stresses or strains in the electronic structure, there seems to be little manifestation of this in the realized bond angles or bond lengths. Here then we look at deviations especially of bond angles from a presumed sp^3 tetrahedral ideal.

A situation with bond-angle strain is nicely illustrated with the case of super-carborane, of Fig. 1. That is, in an ideal icosahedron if one examines the directrices from the center of the polyhedron through two adjacent apices, then the angle may be found to be $\sim 63.4^\circ$, as may be expected to be close to the angles between B—H bonds at adjacent B atoms (around one of the C atoms of $\text{C}_2\text{B}_{10}\text{H}_{12}$). The point is that in the construction of the super-carborane of Fig. 1, the component carboranes are situated at the corners of equilateral (super-) triangles, so that the 63.4° bond angles are in effect distorted to 60° . This bond-angle strain then contributes to a stress energy, entailing a cost so as to decrease the heat of formation. The super-carborane still forms a realizable (super-)

molecule. But if one goes on to consider the possibility of a super-super-carborane (comprised from 12 super-carboranes situated at the corners of a proportionately larger icosahedron), then the stressed inter-super-carborane bonds bring the non-bonded parts of the super-carboranes into closer contact than desirable, and computations reveal* that the energy of stabilization has dropped close to 0.

Particularly when there is angle-strain and consequent stress, one can imagine that the different building block structures in the overall super-structure might tend to move more nearly independently as whole component units. For the 12 carborane units in the super-carborane, of Fig. 1, one might then anticipate a variety of low-frequency vibrational modes corresponding to the motion of the individual carboranes as rigid wholes. The number of such low-frequency modes should entail 3 translations and 3 rotations for each carborane, but with 3 translations and 3 rotations subtracted off for the super-carborane as a whole. That is, we anticipate $(3+3)\times 12 - (3+3) = 66$ low-frequency vibrational modes for our super-carborane – as indeed was found²³, with a notable gap separating these low-frequency modes from the remaining 252 vibrational modes which involve greater extents of internal vibration within the individual carboranes. This idea of “super-structural vibrational modes” was further checked²⁶ via the construction of a long super-nanotube comprised from 240 carboranes, whence a similar low-frequency band now of $(3+3)\times 240 - (3+3) = 1434$ modes was found separated by a significant gap from the remaining 12240 vibrational modes. Densities of state for the two classes of vibrational modes are shown in Fig. 4.

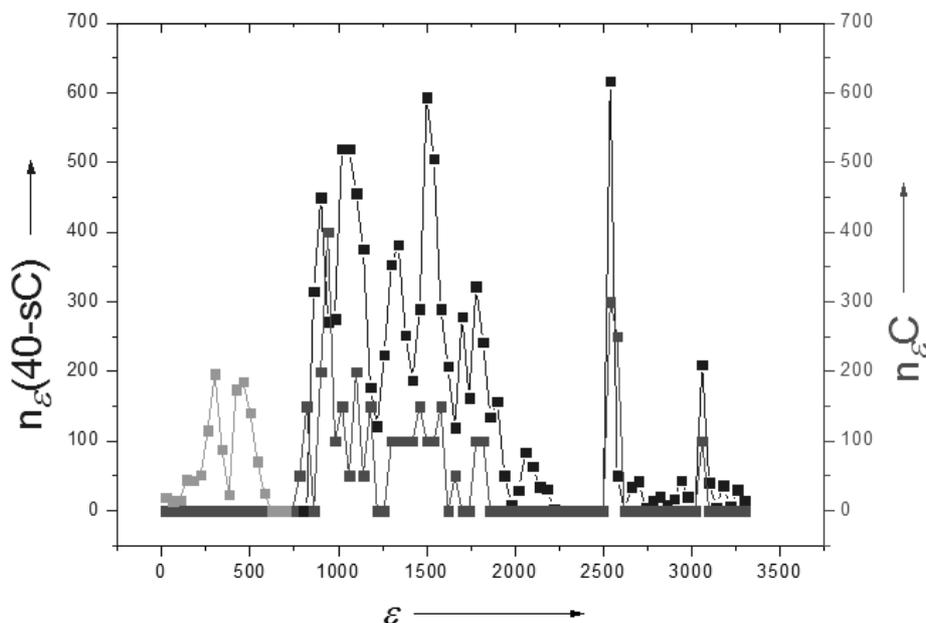


Fig. 4 – Discretized densities of states: $n_{\epsilon}(C)$ in red for a single carborane; and $n_{\epsilon}(40-sC)$ in **green** and **blue** for a 40-unit long super-carborane, consisting of 240 carborane units. The low-frequency super-structural vibrational modes are in **green** for 0 to 700 cm^{-1} (while the “internal” modes in **blue** start at around 900 cm^{-1}).

Presumably with lesser angle-strain, a smaller gap should arise. And the gap would be expected to correlate with an excess stress energy.

BUCKYBALL SUPER-MOLECULES

Another natural choice for a versatile building block would be the C_{60} buckminsterfullerene cage, with 60 points of attachment. Indeed stable linear $(C_{60})_n$ polymers have been known for some time²⁷⁻²⁹, with a mode of interconnection involving a pair of bonds from adjacent C atoms, now involved in tetrahedral (sp^3) bonding. See Fig. 5 for a chain of 6 buckyballs so interconnected. But one naturally might investigate further possibilities involving such interconnections, *e.g.*, Scuseria’s extended sheet³⁰ for a (hypothetical) triangular (super-) lattice of buckyballs. And another example is provided by the experimentally observed^{31,32} cubic (super-) network of buckyballs.

One might also entertain^{33,34} other super-molecular structures, such as super-polyhedra, with C_{60} s at the apices. Indeed it turns out that each of the regular polyhedra can be reasonably so taken as the overall super-skeleton, with very meagre angle strain, beyond that occurring in the (4-membered rings of the) connections in the C_{60} polymer chains. Even the (semi-regular) truncated icosahedron (of C_{60} itself) can be envisaged as a super-skeleton, with negligible such additional angle-strain, whence²⁶

the gap between the super-structural vibrational modes and the remnant more internally involved modes is somewhat smaller than that found in the carborane case.

Another very interesting case is the $(C_{60})_6$ super-octahedron, as illustrated in Fig. 6. There is some angle strain since the angle required for a perfect octahedron is 60° at each corner of a triangular face of the octahedron, whereas the preferred angle for directrices from the center of an undistorted C_{60} to a so connected neighbor (not in a super-cycle) is 60.3° . Particular interest attracts to this super-octahedral species because of a polyradicaloid character anticipated due to the arrangement of the 4 interconnections from one of these buckyballs to its 4 neighbor buckyballs. As indicated in Fig. 7, the 4 interconnections (each via pairs of interbuckyball C—C bonds) isolate a diradicaloid set of 6 π -centers. An easy (theorematic) prediction³⁵⁻³⁶ is of a singlet ground-state. Experimentally this tetramethylene molecular species is observed³⁷ in matrix isolation studies to exhibit a triplet ground state, though it may be that the environment interacts with the structure possibly entailing rotation around the center bond so that the two ends are in orthogonal planes. Notably high quality *ab initio* computations³⁸ support the assignment of a singlet ground state in the (preferred) plane geometry. But despite this controversy concerning the sign of the effective exchange interaction, there is unanimous agreement that the exchange splitting

(between singlet and triplet) should be quite small, so that we anticipate a similar small splitting for this structure embedded in the octahedrally connected C_{60} units. That is, one anticipates a polyradical with $6 \times 2 = 12$ unpaired (or weakly paired) spins, but for which the polyradical should be quite stable, at least kinetically, because (most) all the unpaired electron density should be localized on the inside of the octahedral super-cage

– the external component of the remnant π -network being a quite stable singlet structure (with a Hückel-model HOMO-LUMO gap of $0.31|\beta|$ and 236 Kekule structures). As such this octahedral species should offer the possibility of an isolated single-molecule organic nano-magnet, which would be stable to chemical reaction.

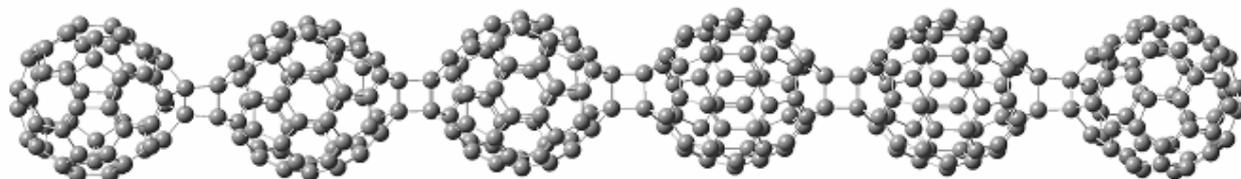


Fig. 5 – Chain of 6 buckyballs so interconnected.

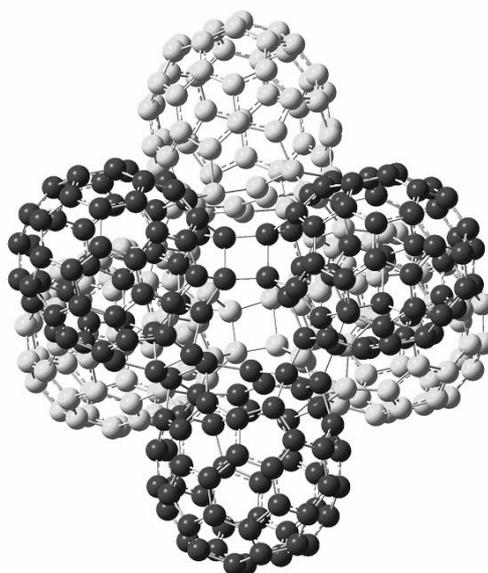


Fig. 6 – The buckyball super-octahedron, with the more intensely colored $(C_{60})_6$ units in the foreground.

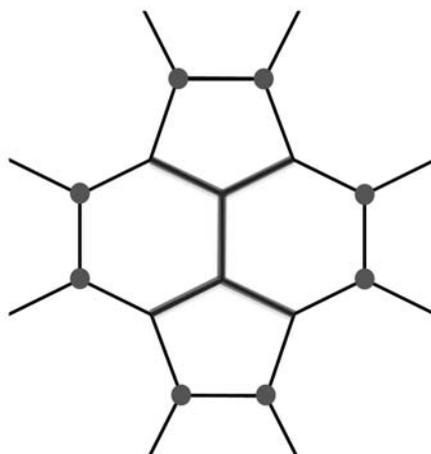


Fig. 7 – The local polyradicaloid π -network in **red**, with the surrounding sites marked in **green** identifying the C-atoms to which the 4 pairs of external bonds (from a C_{60} unit) are to be made to the 4 neighboring buckyballs in our super-octahedron.

CONCLUSIONS

A representative collection of “super-molecules” have been here indicated, with some attention to angle-strain, incumbent stress, and emergent vibrational features. Such might conceivably be useful in the construction of nano-devices. The idea of super-structures with a protected (non-reactive) high-spin interior (like our super-octahedron) seems of potential interest. A suitable criterion for a “super-molecule” might be the occurrence of our partitioning of the vibrational spectra into two pieces: a low-frequency collection of super-structural vibrational modes; and a higher frequency collection of vibrational modes more prominently involving internal molecular distortions.

For many (or most) such super-molecules, there is a serious synthetic challenge. Ideas concerning Bertz's^{39,40} synthetic “complexity” may perhaps be relevant. An intriguing idea occurs with proposals^{15-18,23} of possible “mechano-synthesis” techniques – though in most of these works, it seems that issues of how to overcome strain and stress have not been fully addressed yet. The idea of using DNA scaffolds⁴¹⁻⁴² to guide synthesis is also interesting, and some implementations have been made. Finally besides our indications of super-structures made from a single type of building block, there is of course the possibility of hetero-block components.

The possibilities hopefully will intrigue chemists, such as Sandy Balaban, to whom this article is dedicated.

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