



Icosahedral symmetry super-carborane and beyond



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ABSTRACT

Nano-structures are often sought to be constructed from some especially stable multifunctional unit which can be manipulated into different desired forms. To this end an icosahedral borane or carborane unit is considered as a basic icosahedral building block, to build further larger nano-structures. A potential is noted for the formation of a sort of super-carborane unit, comprised of 12 carboranes at the nodes of a large icosahedron. A further possibility involves taking 12 of these icosahedrons at the corners of an even larger icosahedron, to yield a super-super-carborane structure – perhaps with acetylenic linkages between the super-carborane units.

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1. Introduction

The search for and investigation of novel nano-structures has become an area of ever-increasing importance. One general idea is to consider different multifunctional molecular units available to build up a variety of larger structures. Indeed such was proposed [1] for the icosahedral borane unit, to form 'molecular tinkertoys', with the unit quite rigid, stable, and able to accommodate a few different angles of coupling – offering more possibilities than benzene units for 3-dimensional patterned structures. Indeed some pursuit of different possible simple versatile robust units has been made [2,3]. And occasionally other possibilities for such carborane units have been proposed [4,5]. In the area of nano-technology, different proposed [6] nano-devices have been based on fused diamondoid structures, which however entail a difficult problem for synthesis of the contemplated highly fused (often stressed) structures – and a good deal of experimental effort has been expended [7] to seek to deal with such structures – in part fueled by the discovery [8,9] of a natural source of many polymantanes.

Here we return to Muller et al.'s [1] original dodeca-borane (or carborane) units to see whether some especially novel structures might be constructed. Now $B_{12}H_{12}^{2-}$ is a well-known [10–13] perfectly stable anion, of a fairly unique elegant icosahedral

symmetry. To avoid (unshielded) Coulomb repulsions and thereby facilitate couplings between such icosahedral units it seems plausible instead to work with (the also well-known [11–15]) neutral (iso-electronic) carborane units $C_2B_{10}H_{12}$, which though they do not manifest strict icosahedral symmetry, still entail a (very slightly distorted) molecular icosahedron. Indeed there are 3 isomers depending on where the two C atoms replace B atoms. We focus on the *para*-isomer, as in Figure 1, since in the next stage of construction this leads to an especially highly symmetric structure (and also it is more stable than the *ortho*- or *meta*-isomers). Indeed we propose taking 12 of these *para*-carborane units and coupling them to form a giant icosahedron, in such a way that the C...C axis of a carborane occurs along a 5-fold axis of the giant icosahedron. During the coupling, a pair of B–H bonds in neighboring carboranes are replaced by a B–B bond (with the pair of H atoms being removed). This is to be done at each of the five B atoms surrounding one of the C atoms of $C_2B_{10}H_{12}$. With the indicated mode¹ of coupling, the result should be a new icosahedral symmetry species, of which there are not so many, but including: the dodecaborane

¹ The vertices of a regular icosahedron structures may be elegantly located. To detail this let \mathbf{u}_ξ denote unit vectors along the $\xi = x, y, z$ directions, define the 'golden ratio' $\varphi = (\sqrt{5} + 1)/2$, and let l be the edge (B–B- or B–C-bond) length. Then the 12 vertex positions are $\mathbf{r}_{\xi\zeta}^{\sigma\tau} = l(\sigma\varphi\mathbf{u}_\xi + \tau\mathbf{u}_\zeta)/2$, where σ & τ are + or – and $\xi\zeta = xy, yz, zx$. For the super-icosahedron the new super-edge lengths are $l' = 2r + l$ where $r = \{(5 + \sqrt{5})/8\}^{1/2}l$ is the radius of each of the (12) smaller icosahedra, which are translated to the centers of this larger icosahedron and rotated to interconnect properly.

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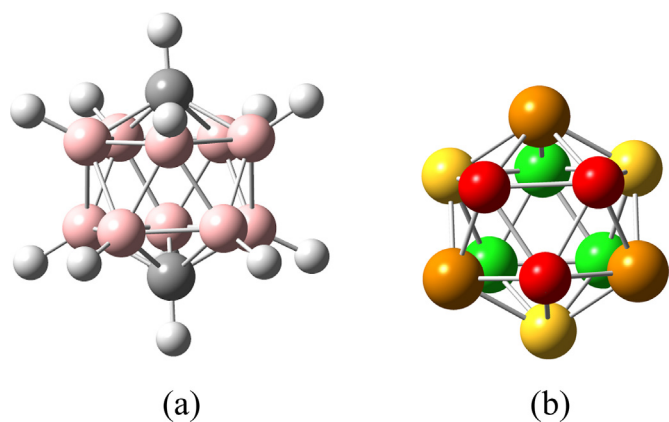


Figure 1. The basic building unit *para*-carborane. Pink, black and white colors represent the boron, carbon and hydrogen atoms respectively in (a). (b) Illustrates an aid to perception of 3-dim structure, with nearest vertices colored red, followed by rainbow colors (orange, yellow, and green) as the distance increases. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

anion; buckminsterfullerene; several other inorganic coordination complexes [16–20]; further fullerenes [1] (though most of these are hypothetical); and several viruses [21–23]. Granted our super-carborane structure, a further conceivable possibility is to take 12 of these new super-carboranes and couple them together to form a super-super-carborane, also of icosahedral symmetry.

2. Super-carborane

The resultant super-carborane ($C_2B_{10}H_7$)₁₂ structure is as in Figure 2, and has been geometry-optimized at the B3LYP/3-21G level of theory. But in fact a theoretical difficulty arises, that the bond angles are not quite right – in that in this construction, triples of carborane units are to form an equilateral triangular face at the super-carborane. That is, the construction demands that inter-unit angles of 60° arise, whereas the angles of two B–H bonds at neighboring sites of a regular icosahedral (car-) borane unit are not directed at this angle, but rather at $\approx 63.3^\circ$. The consequent stress and strain is apparently handled tolerably well at our super-stage. But to check the stresses, more detailed computations of force constants are appropriate. So such were carried out, first at the molecular mechanics level. The lowest frequency super-carborane vibrational force constant is $\sim 190\text{ cm}^{-1}$, which indicates reasonable stability for the species. However, this is significantly less than half the frequency for the beginning carborane whose lowest vibrational force constant is $\sim 790\text{ cm}^{-1}$, which is a manifestation of a wagging of H atoms accompanied by distortions of the attached borons in the boron triangles in the belt of borons around the *para*-C-axis. The lowering of the force constants to that of the super-carborane is plausibly due to stresses arising from the mentioned angle off-set. A check for this has been made via examination of the associated normal modes: we find that this low-frequency mode (at $\sim 190\text{ cm}^{-1}$) involves primarily the near-rigid motion of whole $C_2B_{10}H_7$ units – which is to say it is the bonds between these units which are weak, evidently because of the indicated angle-off-set stress. Moreover, granted such weak inter-carborane

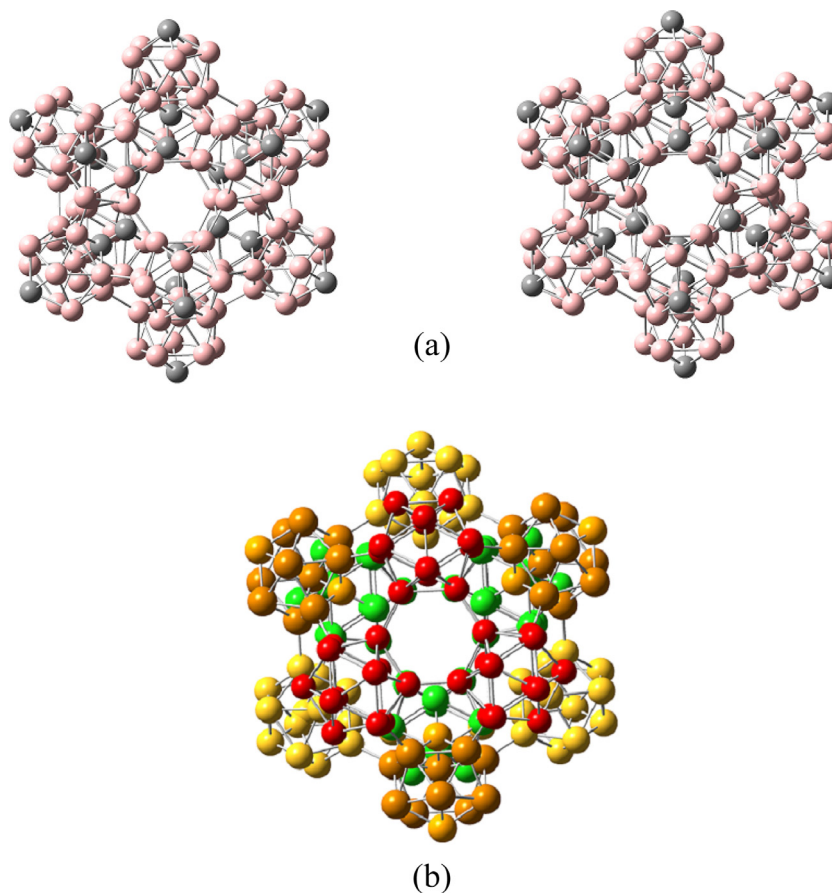


Figure 2. Super-carborane, with H atoms not shown. Left- & right-eye stereo views of the molecule are shown in (a). (b) Again has nearest vertices colored red, followed by rainbow colors (orange, yellow, and green) as the distance increases. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

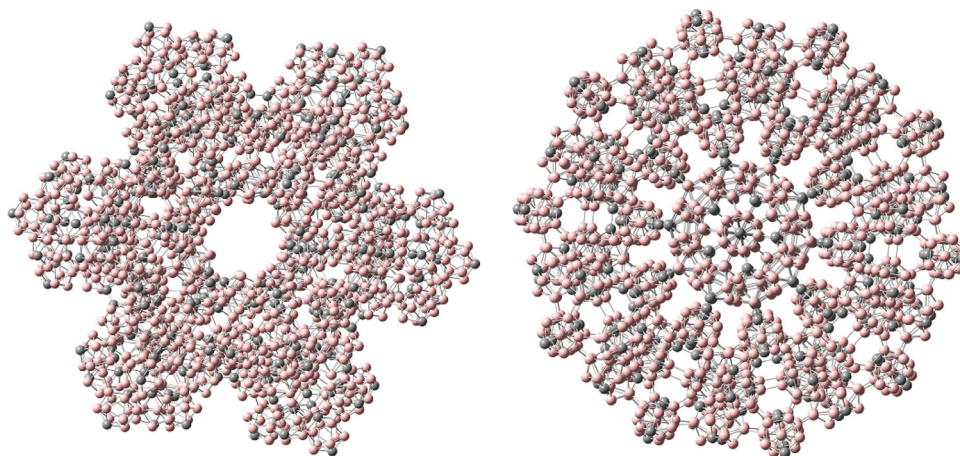


Figure 3. Two views of super-super-carborane, with H atoms not shown.

coupling, there should be many other additional low-frequency modes: 3 rotational and 3 translational modes for each of the 12 carborane units, minus 3 overall translation and 3 overall rotation for the super-carborane as a whole, to give $(3 + 3) \cdot 12 - (3 + 3) = 66$ hypothesized low-frequency vibrational modes. Indeed, we find exactly 66 such low-frequency modes ranging from $\sim 190 \text{ cm}^{-1}$ up to $\sim 480 \text{ cm}^{-1}$ where after there is a jump to $\sim 880 \text{ cm}^{-1}$. Examination of the $\sim 480 \text{ cm}^{-1}$ normal mode reveals that it involves mostly motion of the individual whole carborane units, whereas the $\sim 880 \text{ cm}^{-1}$ normal mode involves H-atom wagging internal to individual carboranes. Thus the super-icosahedron is verified as a stable possibility, manifesting internal stress associated to an ensemble of (66) low-energy normal modes. The behavior seems to be similar to that of molecular crystals (where the internal vibrational modes are of high frequency, while the low-frequency (vibrational) modes involve different comparatively rigid molecules vibrating/rotating against one another).

This just noted result is only for molecular mechanics, so we repeated the computation via DFT, using the B3LYP/3-21G model chemistry. We ended up finding much the same qualitative picture, though with different values for the various frequencies: the lowest frequency was $\sim 120 \text{ cm}^{-1}$ and the 66th was $\sim 350 \text{ cm}^{-1}$, both involving what look to be primarily motions of rigid carboranes – and after that there is a gap of $\sim 100 \text{ cm}^{-1}$ to the 67th level which again involves notable internal motions (within the carborane units). We also did these calculations at other levels of chemistry via semi-empirical, DFT and MP2 methodologies and found that the results are consistent in that the explicated qualitative feature are² independent of method and basis set. All the calculations were made using GAUSSIAN 09 software [24].

² We evaluated the frequencies of the beginning carborane and the super-carborane units other level of theories to test the consistency of our results reported in the text. For the beginning carborane we first calculated the frequencies in the semi-empirical AM1 and PM6 methods and found that the respective lowest vibrational force constants are 204 and 346 cm^{-1} respectively. We again evaluated DFT and MP2 calculations on this moiety involving 6-31G and 6-311+G(d,p) basis sets by these two methodologies. The results are 433, and 463 cm^{-1} in DFT and 442, and 488 cm^{-1} in MP2 with those two corresponding basis sets. For the super-carborane molecular cluster we again tried semi-empirical AM1 and PM6 level of calculations. And our results show that the first vibrational force constants are 119 and 101 cm^{-1} , whereas its 66th components are 299 and 281 cm^{-1} and the next 67th components are further high at 328 and 318 cm^{-1} respectively by those methods respectively. The results stated above are consistent with our earlier (molecular mechanics) results reported in the text.

3. Super-super-carborane

Despite the stress in the super-carborane, we have also constructed (from 12 super-carboranes) the super-super-carborane structure $[(\text{C}_2\text{B}_{10}\text{H}_7)_7(\text{C}_2\text{B}_{10}\text{H}_6)_5]_{12}$ of Figure 3, with geometry optimization just via molecular mechanics. Here the couplings between super-carboranes are by way of C–C bonds. Again the resultant super-super-carborane seems also to be of icosahedral symmetry. But upon examination of the normal mode frequencies (at the molecular-mechanics level), we find two force-constants at ~ 0 frequency – although, if nothing else, dispersion interactions should make a bound state. Still it seems that (at least at this level of theory) the stress has become so severe that the proposed molecule seems unlikely to manifest any reasonably stable minimum corresponding to our super-super polyhedron.

In as much as the straight-forward super-super-carborane appears to lack stability, we tried another strategy to relieve the stress involved with the mismatch of bond angles. In

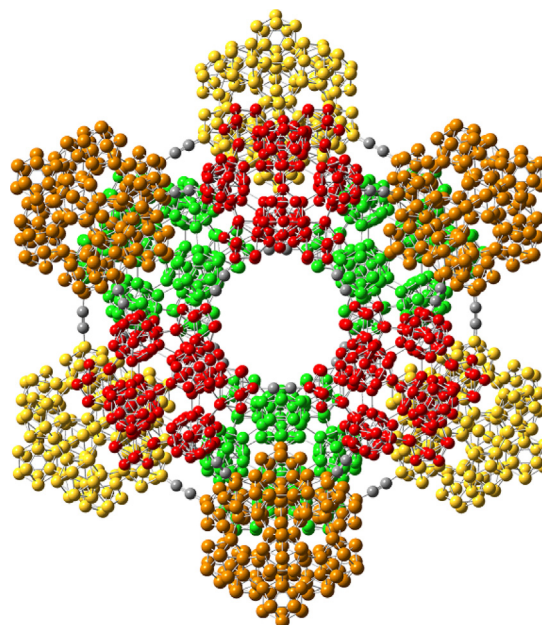


Figure 4. Super-acetylenic-super-carborane, with H atoms suppressed. Again the nearest vertices are colored red, followed by rainbow colors (orange, yellow, and green) as the distance increases. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

place of a single C–C bond interconnecting a pair of super-carboranes, we placed there instead an acetylenic linkage C–C≡C–C (with the two terminal C atoms here being part of two different component super-carborane units). This novel species [(C₂B₁₀H₇)₇(C₂B₁₀H₆)₅]₁₂[C≡C]₃₀ has a bonding arrangement between super-carborane units which prefers a linear geometry,³ though there is a greater distance over which to distribute the stress and strain arising from the angle mismatch. The structure is found in Figure 4. Notably in this case (at the molecular-mechanics level) we find all force constants to be positive. The lowest is at ~22 cm⁻¹, and if we follow the frequencies up to the 66th it turns out to be at ~70 cm⁻¹, with a gap to the 67th at ~180 cm⁻¹. That is, the 12 different super-carborane units to a first approximation seemingly move as single units—with part of the reason for diminishing frequencies being the increase in mass of such units. This case evidently results in a stable species.

4. Conclusion

We have investigated the possibility of novel nano-structures comprised from borane or (more feasibly) neutral carborane units. Though the species presents a seemingly severe synthetic challenge, the super-carborane appears quite stable. It manifests a collection of 66 low-frequency modes involving motions of primarily near-rigid carborane units – after these low-frequency modes there is a gap to modes involving internal distortions within carborane units. The straight-forward extension to the super-super-carborane seems to give a structure so severely stressed as to be experimentally quite questionable, unless we insert acetylenic linkage spacers. This linkage-spaced super-super-carborane manifests again a new gap of 66 low frequency modes, evidently manifesting our picture of whole units (now super-carboranes) moving as a whole. One could imagine iteration to even further stages, of super-super-super-carboranes, and then beyond toward a fractal [25] limit⁴ – but because of the angle mismatch, one would presumably need to insert ever longer spacer units to relieve stresses – one candidate for such spacers being poly-acetylenes (by which we mean poly-ynes). The super-carborane manifests a sizable cavity in which it is conceivable that various molecules can be trapped, and the super-super-carborane species an even larger

cavity (albeit also with larger holes in the faces). That is, especially upon iteration, a range of sizes of cavities would result. The super-carborane and super-super-carboranes are of a uniquely elegant icosahedral symmetry.

Acknowledgments

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³ The distance between adjacent super-carborane centers now, instead of being $l' = 2r + l$, becomes $l' = 2r + 2l + l_{\equiv}$ where l_{\equiv} is the length of a C≡C triple bond. It should also be noted that the super-super-carborane distances l' (either with or without the acetylenic unit) are predicated on unstrained bond angles, which of course is not correct, so that these formula are just approximate – and indeed a similar comment applies even for the super-carborane.

⁴ To iterate the construction relieving stress, the lengths of the polyacetylene chains would need to increase in proportion to the size of the previous stage unit. That is, if the radius of a unit at stage s is r_s , then the number of acetylene units at the s th stage would need to be proportional to r_{s-1}/l . If one were just imagining contact between sphere units, then the radii would go up as $r_s \approx \{2[(5 + \sqrt{5})/8]^{1/2}\} r_{s-1}$ which is to say as $r_s \sim \{(5 + \sqrt{5})/2\}^{1/2} r_{s-1}$. But with a number $f \cdot r_{s-1}/l$ of acetylene units added between such spheres, one has instead $r_s \sim \{(5 + \sqrt{5})/2\}^{1/2} + f$. As the acetylene chains are so narrow in comparison to the units interconnected, the polyacetylene chains contribute negligibly to the mass m_s in the high- s limit. That is, $m_2 \approx 12 \cdot m_{s-1}$ and $m_s \sim 12^s$. The fractal dimension d is [25] then the value for which the density m_s/r_s^d approaches a nonzero finite limit as $s \rightarrow \infty$, which is to say that $d = \log 12 / \log \{[(5 + \sqrt{5})/2]^{1/2} + f\}$. For a choice of $f \approx 0.8$ (i.e., making the polyacetylene chain just a bit shorter than the radii of the units it interconnects) one then has $d \approx 2.5$.