XIX SBQT
Simpósio Brasileiro de Química Teórica 2017
12 a 17/Nov, 2017, Águas de Lindóia/SP, Brasil

Nugget Hydrocarbons C_nH_n with Six Four-membered Rings and their growth as 3D-Scaffolds

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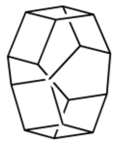
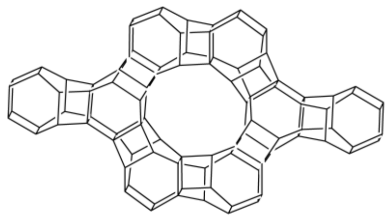
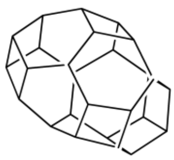
Abstract: Polyhedral hydrocarbons of general formula C_nH_n constitute an important class of compounds, that can be either platonic hydrocarbons, prismanes, form cages, etc. Interest in these compounds arise from their distinct physical properties, chemical reactivities and possible applications in energy storage materials[1,2], in biology, in pharmacology, etc. A special class of polyhedral hydrocarbons, we call nuggets, is comprised of those containing only four- and six- membered rings[3]. It can be easily demonstrated from Euler's polyhedron formula that all such polyhedra must contain exactly six four-membered rings, for an arbitrary number of six-membered rings, with one sole exception: there are no such polyhedra with only one six-membered ring. In this work, we examined all 17 nuggets starting from cubane, with no six-membered rings, up to the one with 28 carbon atoms and 10 six-membered rings. Of these 17, only cubane (C_8H_8), we call Nugget8, has been synthesized in 1964 [4]. A few others have been devised theoretically and had some of their properties computed: Nugget12, Nugget20a, and Nugget24a. As far as we know, all others are being introduced for the first time in this work, and have never been considered in chemistry, not even theoretically. Of these, 3 of them are space filling polyhedral voxels: the cube (Nugget8), the hexagonal prism (Nugget12), and the truncated octahedron (Nugget24a). They are called voxels because they can fill the space completely and can be considered a value in a regular grid in 3-dimensional space; their 2D counterpart being pixels in a bitmap. All nuggets can be fused together in several manners, either through their square faces, or through their hexagonal faces, to generate 3D-scaffolds that can grow indefinitely and that can serve as templates to lead to an enormous number of compounds, either regular or amorphous, space-filled, cage-like, etc. Moreover, the three voxels, in principle, point in the direction of three new allotropes of carbon. In this work, we generated all 17 nuggets, which are the only ones that exist up to 28 vertexes, and calculated their thermodynamic properties in order to verify the likelihood of their existence. Our results indicate that only one of the nuggets seems to be unstable to dissociation: Nugget12, the hexagonal prism, which should easily dissociate into two benzenes, for which RM1 indicates the enthalpy of reaction: $C_{12}H_{12} \rightarrow 2C_6H_6$ to be Δ_rH = -39kcal. This qualitative result has been confirmed by B3LYP/cc-pVDZ which yielded Δ_rG = -148 kcal. This result indicates that the allotrope of carbon constituted by

a 2D expansion of six membered rings chemically bound in the third dimension by single bonds would easily dissociate into layers of graphite. The other carbon allotrope made by a 3D expansion of cubes of carbon is stable towards dissociation, but would contain an enormous amount of strained carbon-carbon bonds, so much so that it could constitute a reservoir of energy if ever made. Besides, it would constitute a super dense allotrope of carbon, with a higher density than diamond. The final one, based on Nugget24 would lead to a viable allotrope which has been already found: carbon sodalite [5]. All nuggets had their thermodynamic properties computed by RM1 and B3LYP/cc-pVDZ. Results indicate that, with the exception of Nugget12, all others are found to be stable and likely to exist. Their RM1 average enthalpy of formation per CH bond, is found to range from 6 kcal.mol^{-1} for Nugget14 to 2,23 kcal.mol^{-1} for Nugget28c. Furthermore, their structures are found to be nicely rigid, adding to the interest in their eventual discovery, with their RM1 lowest vibrational frequency for Nugget28c with 28 carbon atoms being 144 cm^{-1}, which compares with the one for linear $C_{28}H_{58}$ of only 2cm^{-1}. Of the 17 nuggets, 3 are chiral. The nuggets can further fuse together through their square of hexagon faces to form the 3D-scaffolds. Disconsidering the cases of cubane and the hexagonal prism, for the other nuggets studied, the enthalpy of reaction for the fusion of squares with the release of a cyclobutane ranges from 47 kcal.mol^{-1} to -12 kcal.mol^{-1} and for the fusion of two hexagons with the release of a cyclohexane ranges from 33 kcal.mol^{-1} to -37 kcal.mol^{-1}. Examples of symmetric and asymmetric 3D-scaffolds made out by fusion of 8 Nugget16s and 4 Nugget26s are shown below.

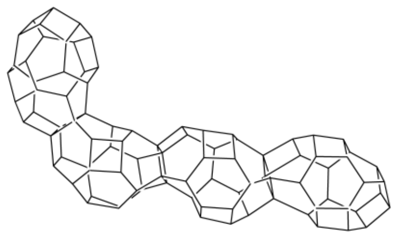


Nugget 16





Nugget 26



Key-words: Hydrocarbons, prismanes, carbocyclic cage compounds
Support: CNPq, FACEPE, PRONEX.

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