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SMALL FULLEROIDS

MIRCEA V. DIUDEA[a] and IOAN SILAGHI-DUMITRESCU[b]

[a, b] *Faculty of Chemistry and Chemical Engineering*
Babes-Bolyai University, 3400 Cluj, Romania
diudea@chem.ubbcluj.ro; isi@chem.ubbcluj.ro

ABSTRACT. Novel small fulleroids were "in silico" synthesized by enlarging some Archimedean well-known polyhedra. The energetic stability and topological characterization of such pure carbon cages is discussed.

INTRODUCTION

A fullerene is an all-carbon molecule in which the atoms are arranged on a pseudospherical framework made up entirely of pentagons and hexagons. "Nonclassical" extensions to include rings of other sizes have been considered[1,2] and may be competitive in energy with the classical fullerenes.

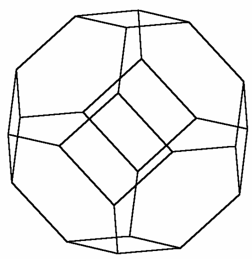
The initial fascinating appeal, coming from their beautiful symmetry[3-5] shifted later to real chemistry.[6-8] Carbon allotropes with finite molecular cage structures have been functionalized or inserted in supramolecular assemblies.[9-11] Besides the well known near-spherical fullerenes, cylinders, capped tubules and tori have aroused both theoretical and experimental interest.[12-20] Multi elemental large cages have also been studied.[21]

EXTENDED ARCHIMEDEAN CAGES

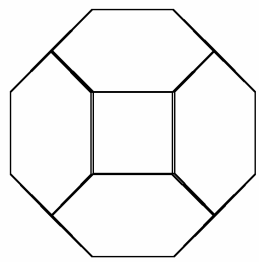
In addition to the earlier five Platonic polyhedra: the tetrahedron (T_d), cube (O_h), octahedron (O_h), dodecahedron (I_h), and icosahedron (I_h), other 13 elegant objects, resulting mainly by a truncation operation, are due to Archimede.[22] Two of them attracted our attention: the truncated octahedron (O_h) and truncated cuboctahedron (O_h), (OT4 and COT4, respectively) in connection with some successful synthesis of phenylenes, organic compound having alternating sequence: C_4, C_6.[23,24]

Our goal was the building of some cubic cages (*i.e.*, trivalent cages), originating in (or related to) the above two Archimedean objects, keeping in mind that the smallest cage obeying the "12 pentagon" definition of fullerenes is just the dodecahedron. Semiempirical AM1 calculations, performed by the HyperChem[25] software package, were aimed to give information on the energetic stability of such all-carbon cages, possibly appearing in the synthesis of fullerenes. By enlarging the polar ring from 4 up to 8, families of cages are generated. In the following we illustrate the cages and give semiempirical and spectral (see below) data in tables for each family.

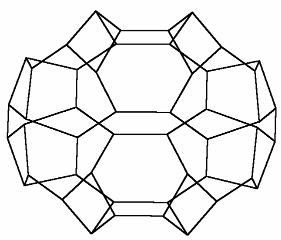
OT4; (D_{4h}); *N* = 24 (side)



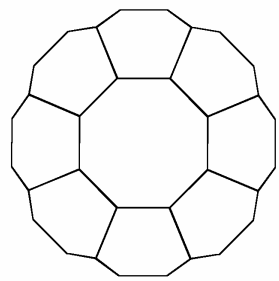
OT4 (top)



OT8; (D_{8h}); *N* = 48



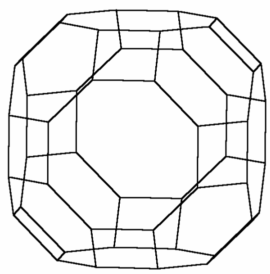
OT8; (top)



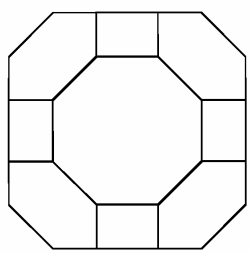
	Cage	*N*	Sym.	AM1 HF/atom	AM1 GAP	Spectral Data			
						$\lambda_{N/2}$	$\lambda_{N/2+1}$	GAP	Shell
1	OT5	30	D_{5h}	33.044	6.4437	0.4772	-0.4142	0.8914	PC
2	OT6	36	D_{6h}	35.068	6.5199	0.4142	-0.4142	0.8284	PC
3	OT7	42	D_{7h}	45.213	2.5661	0.3922	-0.4142	0.8064	PC
4	OT8	48	D_{8h}	47.584	-	0.4142	-0.4142	0.8284	PC

PC = properly closed shell

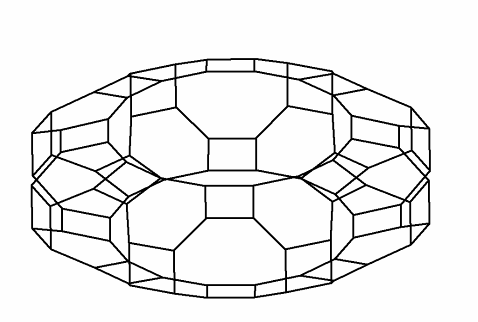
COT4; (C_{4h}); *N* = 48 (side)



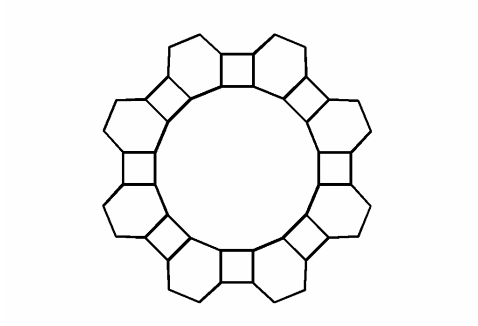
COT4 (top)



COT8; (C_{8h}); N = 96 (side)



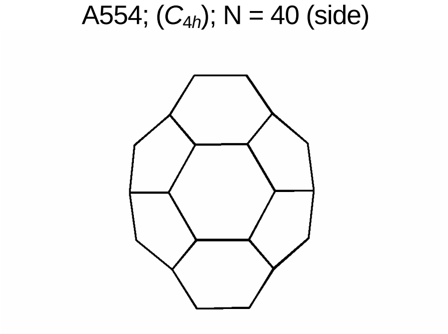
COT8 (top)



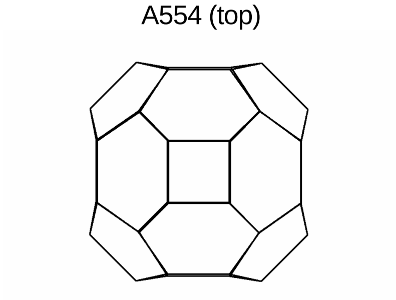
	Cage	N	Sym.	AM1 HF/atom	AM1 GAP	Spectral Data			
						$\lambda_{N/2}$	$\lambda_{N/2+1}$	GAP	Shell
1	COT5	60	C_{5h}	29.275	1.6354	0	0	0	OP
2	**COT6**	72	C_{6h}	28.907	5.6600	0	0	0	**M**
3	COT7	84	C_{7h}	30.934	5.4804	0	0	0	OP

OP = open shell; M = metallic shell

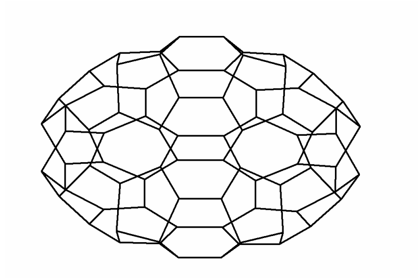
A554; (C_{4h}); N = 40 (side)



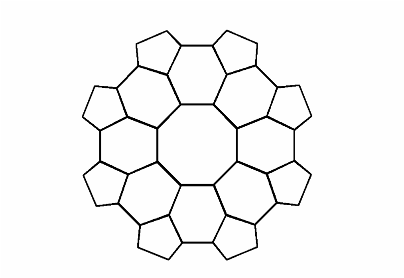
A554 (top)



A558; (C_{2v}); N = 80 (side)



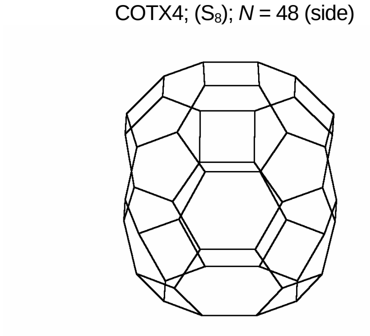
A558 (top)



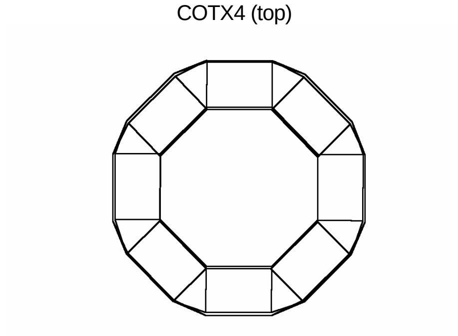
	Cage	N	Sym.	AM1 HF/atom	AM1 GAP	Spectral Data			
						$\lambda_{N/2}$	$\lambda_{N/2+1}$	GAP	Shell
1	A555	50	C_S	20.425	4.8581	0.4142	0.3111	0.1031	PSC
2	A556	60	C_{2h}	20.379	5.5507	0.4142	0.3111	0.1031	PSC
3	A557	70	C_1	24.076	6.0451	0.4142	0.3111	0.1031	PSC
4	A558	80	C_{2v}	30.134	6.6226	0.4142	0.3111	0.1031	PSC

PSC = pseudoclosed shell

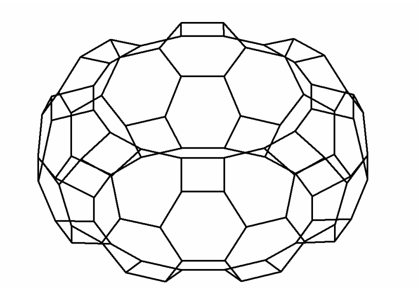
COTX4; (S_8); N = 48 (side)



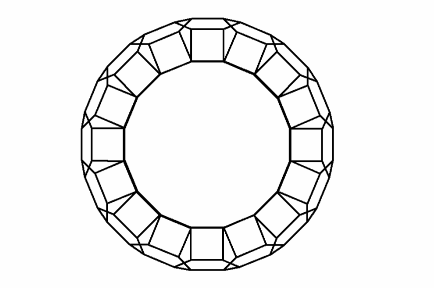
COTX4 (top)



COTX8; (S_{16}); N = 96 (side)



COTX8 (top)

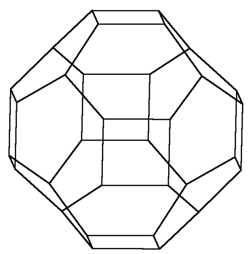


This family is derived from COT by a twist-1 coupling.

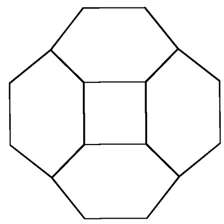
	Cage	N	Sym.	AM1 HF/atom	AM1 GAP	Spectral Data			
						$\lambda_{N/2}$	$\lambda_{N/2+1}$	GAP	Shell
1	COTX5	60	S_{10}	24.591	4.9335	0	0	0	OP
2	COTX6	72	S_{12}	24.891	4.6341	0	0	0	OP
3	COTX7	84	S_{14}	26.000	4.3729	0	0	0	OP

OP = open shell

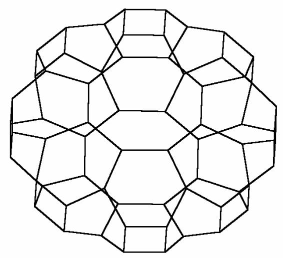
AA4; (D_{4h}) N = 32 (side)



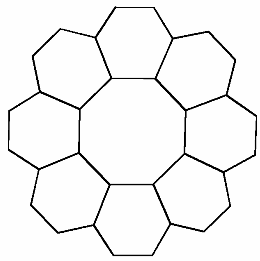
AA4 (top)



AA8; (D_{8h}); N = 64 (side)



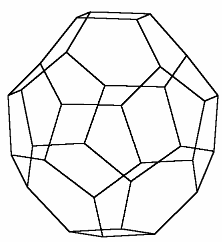
AA8 (top)



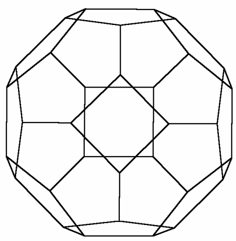
	Cage	N	Sym.	AM1 HF/atom	AM1 GAP	Spectral Data			
						$\lambda_{N/2}$	$\lambda_{N/2+1}$	GAP	Shell
9	AA5	40	D_{5h}	30.202	3.3198	0.2056	0	0.2056	PC
10	AA6	48	C_1	30.949	5.2355	0	0	0	OP
11	AA7	56	D_{7h}	39.484	1.8858	-0.0612	-0.0612	0	OP
12	**AA8**	64	D_{8h}	43.246	5.8994	0	0	0	**M**

PC = properly clossed shell; OP= open shell; M = metallic shell

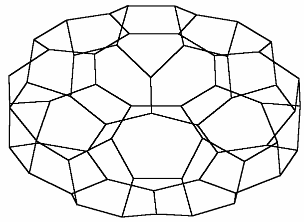
AAX4; N = 32 (side)



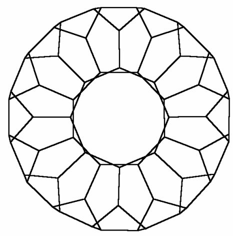
AAX4 (top)



AAX8; (D_8); N = 64 (side)



AAX8 (top)



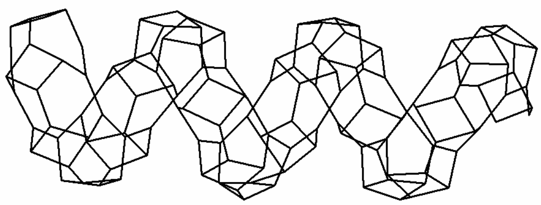
Note that this family is obtained by a twist -1 coupling performed on the above AA family.

	Cage	N	Sym.	AM1 HF/atom	AM1 GAP	Spectral Data			
						$\lambda_{N/2}$	$\lambda_{N/2+1}$	GAP	Shell
1	AAX5	40	C_1	24.311	2.1470	0.4865	0.1133	0.3732	PSC
2	AAX6	48	D_6	25.789	6.1145	0.4142	0.2007	0.2135	PSC
3	AAX7	56	D_{7d}	31.374	6.6641	0.4856	0.1851	0.3005	PSC
4	AAX8	64	D_8	38.821	6.9308	0.4444	0.1559	0.2885	PSC

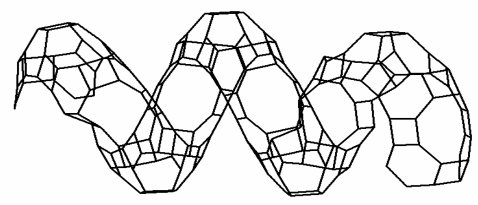
PSC = pseudo clossed shell

In cages with larger polar rings, the strain is so high that a cross-section cutting results in more stable spiral objects (see the two spirals, corresponding to the OT and COT families). This tendency appears by examination of the semiempirical data: an increase in the heat of formation, in going to larger polar rings, is observed. Spiral structures have been reported by the group of Volhardt.[23,24]

OT11spiral, N = 132;



COT16 spiral; $N = 192$



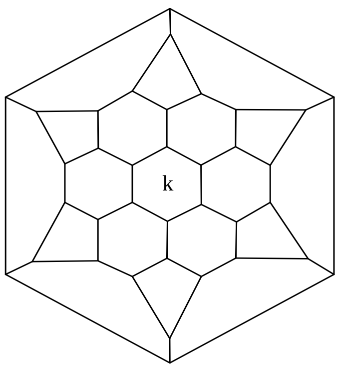
SCHLEGEL PROJECTION OF RELATED ARCHIMEDEAN CAGES

A graph is said to be embedded in a surface *S* when it is drawn on *S* so that no two egdes intersect.[26] A graph is planar if it is embeddable in the plane (or in the sphere). Any spherical polyhedron obeys the Euler theorem:[27]

$$V - E + F = 2 \qquad (1)$$

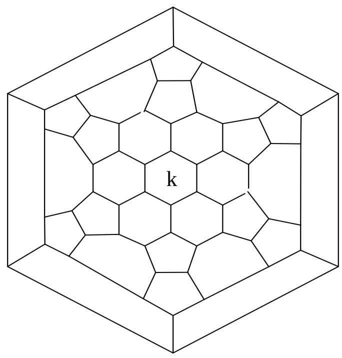
The graph associated to a polyhedron, consisting of its vertices *V*, edges *E* and faces *F*, is a planar map, and clearly satisfies relation (1). Thus, a polyhedron can be drawn on the plane as a Schlegel progection. We use this representation in the case of our extended Archimedean polyhedra, as illustrated below. In the top of each Schlegel diagram, the point group symmetry and spiral code[28,29] are given. The spiral sequence starts from the polar ring (of size *k*) and finishes to the opposite pole.

OT*k*; (D_{kh})
$k\ 6_k\,(4\ 6)_k\ k$



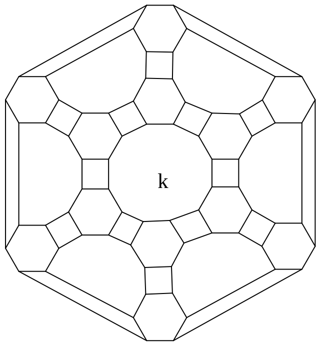
COT*k*; (C_{kh})

A55*k*; k = 5; 6 (fullerene)
$k\ 6_k\,(5\ 6)_k\,(5\ 6)_k\ k$

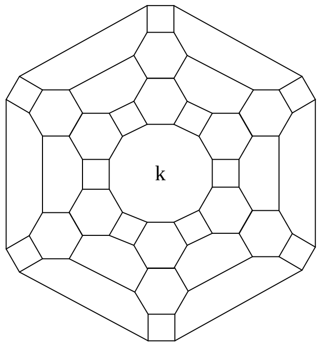


COTX*k*; (S_{2k})

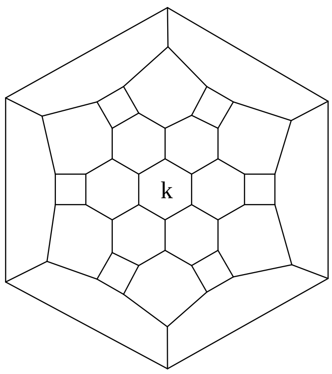
$2k\ (4\ 6)_k (4\ 8)_k\ (4\ 6)_k\ 2k$



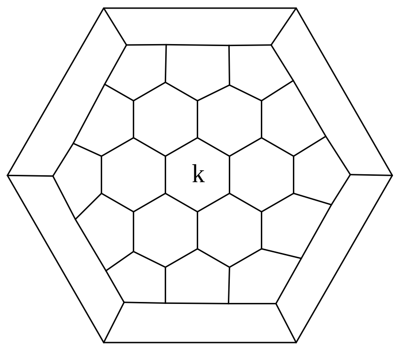
$2k\ (4\ 6)_k (6\ 6)_k\ (4\ 6)_k\ 2k$



AA*k*; (D_{kh})
$k\ 6_k (4\ 6)_k\ 6_k\ k$



AAX*k*; $k = 5; 6$ (fullerene); (D_k)
$k\ 6_k 5_{2k}\ 6_k\ k$



DISCUSSION

The semiempirical data indicate an increase in the heat of formation in going to larger polar rings. The cross-section cut performed on such cages leads to spiral objects. Spiral structures have already been synthesized in phenylenes.

The topology of polyhedral cages herein designed could be rationalised by the spiral code:[28,29] the polar ring size *k* is the generalizing parameter.

Some of the proposed polyhedra belong to the classical fullerenes: A55*k*; *k* = 5; 6 (A555, *N* = 50, HF = 20.425 kcal/mol; A556, *N* = 60, HF = 20.379 kcal/mol) and AAX*k*; *k* = 5; 6 (AAX5, *N* = 40, HF = 24.311 kcal/mol; AAX6, *N* = 50, HF = 25.789 kcal/mol). Their AM1 HF is, however, far from that of C_{60}, of 16.208 kcal/mol.

The HOMO-LUMO gap is a measure of the kinetical stability; a value around 6 eV would be satisfactory. This desiderate is approached by the k = 6 members of the studied objects. In the spectral theory,[30] the type of the band gap is used to classify the π-electronic shell of the molecules: properly clossed shells are expected for the isolable fullerenes, such as C_{60}.

From the above data, it appears that none of the extended Archimedean cages can be considered candidates to the real fullerene status.

CONCLUSIONS

Two of the Archimedean polyhedra: the truncated octahedron (O_h) and truncated cuboctahedron (O_h), have been extended in view of finding information on the thermodynamic and kinetic stability of the derived polyhedra (some of them having alternating sequence: C_4, C_6, as in phenylenes). Related polyhedral cages have also been designed. The conclusion of this study is the following: even the modelled cages hardly compete the already synthesized C_{60} molecule, but they can be useful in understanding the possibility of synthesis of some non-classical fullerenes and/or related structures.

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