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Rhombellane-Related Crystal Networks

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ABSTRACT

Rhombellanes are mathematical structures existing in various environments, in crystal or quasicrystal networks, or even in their homeomorphs, further possible becoming real molecules. Rhombellanes originate in the $K_{2,3}$ complete bipartite graph, a tile found in the linear polymeric staffanes. In close analogy, a rod-like polymer derived from hexahydroxy-cyclohexane, HHCH, was imagined. Further, the idea of linear polymer synthesized from dehydro-adamantane, DHAda, was extended in the design of a three-dimensional crystal network, called here Ada-Ada, of which tile is a hyper-adamantane (an adamantane of which vertices are just adamantanes). It was suggested that Ada-Ada would be synthesized starting from the real molecule tetrabromo-adamantane, by dehydrogenation and polymerization. The crystal structures herein proposed were characterized by connectivity and ring sequences and also by the Omega polynomial.

1. INTRODUCTION

The Rhombellanes are structures with all strong rings being rhombs/squares (Figure 1, left); they have been proposed by Diudea in 2017 [1]. Rombellanes are structurally related to [1,1,1]propellane, an organic molecule, first synthesized in 1982 [2]; by IUPAC rules [3], it is named tricyclo[1.1.1.0^{1,3}]pentane, a hydrocarbon with formula C_5H_6, containing

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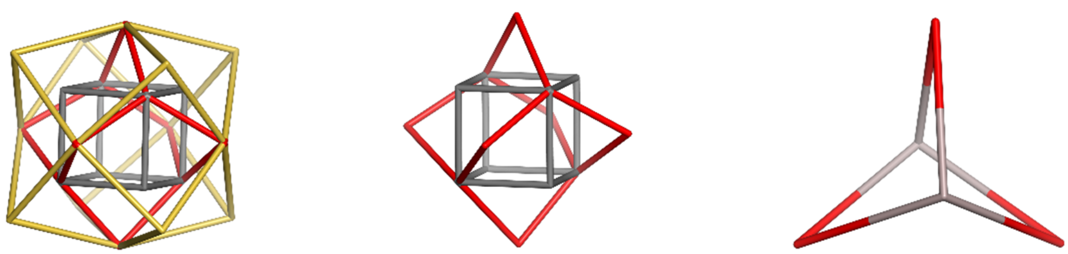
only triangles; its reduced form, C_5H_8, eventually named bicyclo[1.1.1]pentane, has only rhomb/square rings; it can be represented as $K_{2,3}$ - the complete bipartite graph (Figure 1, right). [1,1,1]Propellane undergoes spontaneous polymerization, to bicyclo[1.1.1]pentyl oligo- and polymers (degree of polymerization up to 100), called [n]staffanes [4,5]; they are rigid, linear structures (Figure 2, left), molecular rods that exhibit restricted rotation along the rod axis.

A rhombellane was defined by Diudea [6-8] as a structure having:

a) *All strong rings are rhombs/squares;*
b) *Vertex classes consist of all non-connected vertices;*
c) *Omega polynomial has a single term:* $1x^{|E|}$*;*
d) *Line graph of the parent graph has a Hamiltonian circuit*;
e) *It contains at least one* $K_{2.3}$ *subgraph.*



Cube-rhombellane.22 ADA-rbl(C).14 $K_{2.3}.5 = Rh_{2(3\times1)}.5$

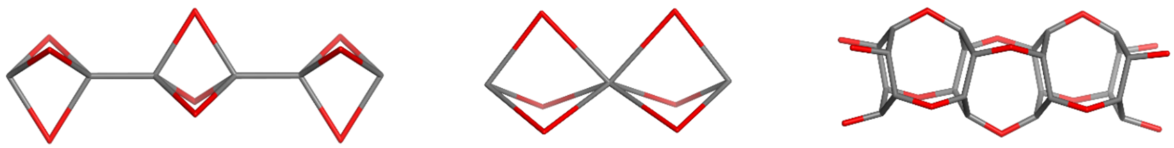
Figure 1. Rhombellane basic structures.

Construction of the cube-rhombellane (Figure 1, left) is illustrated in Figure 1. Each square face forms a $K_{2.3}$ motif (Figure 1, middle and right) by joining the opposite corners with homeomorphic diagonals; these diagonals are joint together in an adamantane motif (Figure 1, middle, the red contour); $K_{2.3}$ and adamantane are both "tiles", not polyhedra.

Rhombellanes are, in general, designed by the "rhombellation" operation; it starts with diagonalizing each face of an all-rhomb map Rh_0 by a joint point (a "rbl"- vertex); then, new vertices are added opposite to the parent vertices and join each of them with the rbl-vertices lying in the proximity of each parent vertex, thus local Rh-cells being formed. The process can continue, considering the envelope Rh_n as "Rh_0" for Rh_{n+1}, in this way shell by shell being added to the precedent structure. Since the two diagonals of a rhomb may be topologically different, each generation may consist of two isomers.

The cube-rhombellane.22 (Figure 1, left) has the vertex connectivity 6 and 3, respectively. To synthesize it as a molecule, one may start from 1,2,3,4,5,6-Hexahydroxy-cyclohexane HHCH, to provide the connectivity 6; connectivity 3 is more accessible [9,10].

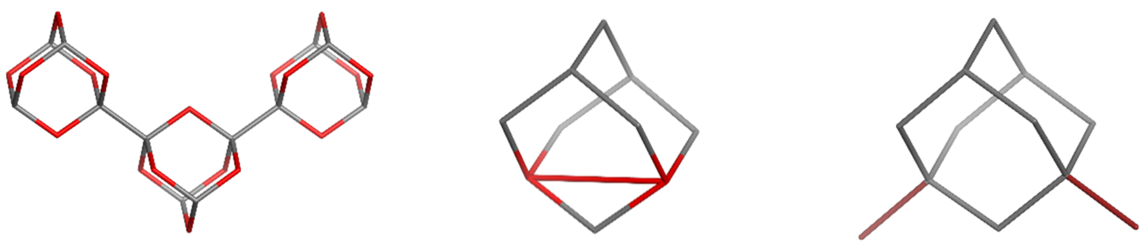
By analogy to [1.1.1]propellane and staffanes [*n*]stf [5], a linear rod-like polymer [*n*]HHCH (a poly-ether) was designed by Diudea (Figure 2, middle and right).



[3]Stf(4) [2]Stf(6) [3]HHCH(6)

Figure 2. Rhombellane-related linear polymeris structures (in square brackets is the number of building blocks; in round brackets is the connectivity of bridge-points).

This analogy was also exploited in the synthesis of linear ("zig-zag") polymer of which building block is 1,3-dehydro-adamantane (Figure 3, left - named here [3]DHAda, with the staffane system). Adamantane Ada molecule was discovered by Landa (a Czech chemist) in 1933 in petrol [11]; then a series of syntheses of Ada and its derivatives have been proposed [5,12-14]. Dehydro-adamantane DHAda (Figure 3, middle) is obtained by eliminating the two bromine atoms from 1,3-dibromo-adamantane (Figure 3, right).



[3]DHAda oligomer Dehydro-Ada (DHAda) Dibromo-Ada

Figure 3. Adamantane derivatives.

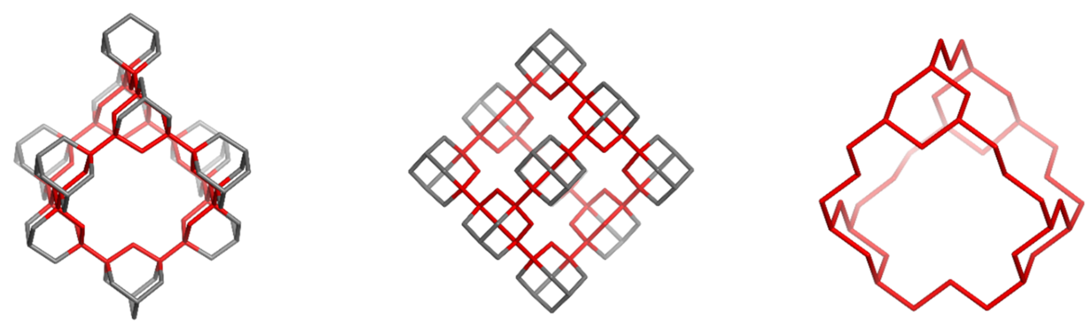
2. Results

According to Steinhardt [15], crystals are highly ordered structures, with atomic clusters repeated periodically, in three independent directions of the space, and showing an essentially discrete diffraction diagram; there are only 14 ways to build the crystal structures, namely the Bravais lattices; they are completely described by the 230 symmetry groups of the space.

2.1. Ada–Ada Crystal Network

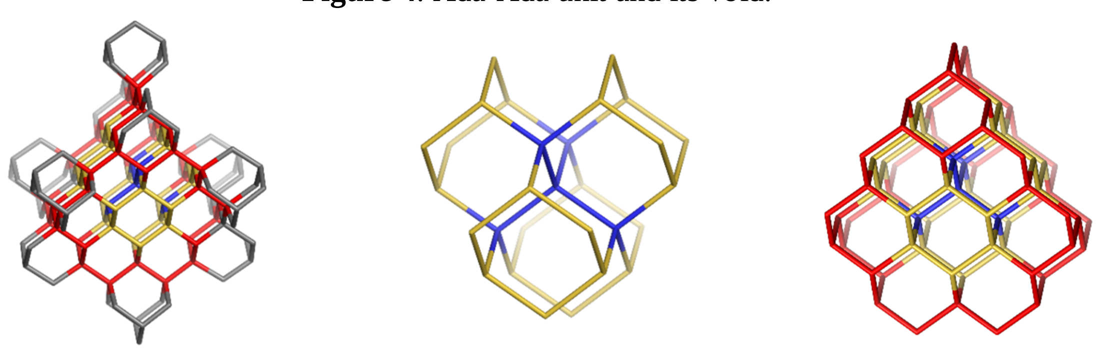
A hypothetical tetra-dehydro-adamantane TDAda molecule, obtainable by eliminating the four bromine atoms in tetraboromo-adamantane, is conceivable to undergo a 3D-polymerization, to provide a triple-periodic crystal network, eventually named Ada-Ada, as Diudea designed.

The 3D Ada-Ada net has the building block, i.e. tile [16], a hyper-adamantane (the structure of adamantane (i.e. tricyclo[3.3.1.1$^{3.7}$]decane, by IUPAC nomenclature [3]) in which all atoms are changed by Ada), named here Ada-Ada.100 (Figure 4, left). It has a tetrahedral symmetry, as the basic adamantane; Ada-Ada and its void (Figure 4, right) can be perfectly filled by the Dia net, as in Ada-Dia.129 (Figure 5, left); the missing part of Dia net (space group Fd-*3m*), Dia.29 (Figure 5, middle), consists of four Ada units sharing a common (central) point (in blue, Figure 5, middle). Thus, the Ada-Ada net is a kind of Dia net, with defects, namely Dia.29, repeated at a distance of about 0.7.1 nm (from a central point to the other), as shown in Figure 6. The Filled-Void (Ada-Ada).71 (Figure 5, right) is a tetrahedral tile, with faces having six Ada-units (each shared by two faces), the core of four Ada and the corners by four Ada, a total of twenty Ada units. Ada-Dia.129 filled tile (Figure 5, left) has additional ten Ada, a total of 30 Ada units.



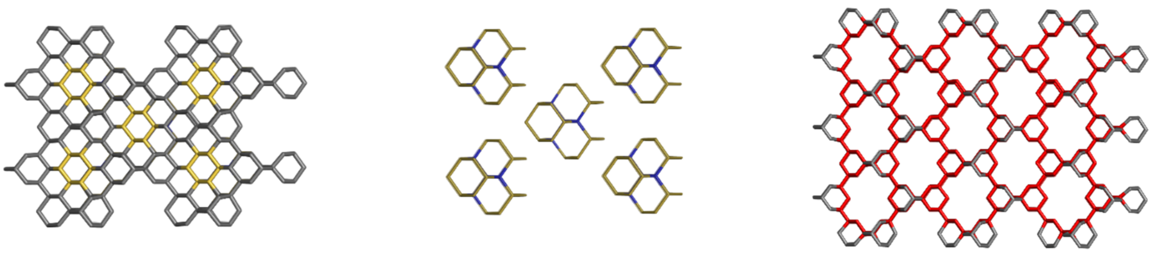
Ada-Ada.100 Ada-Ada.100 (projection) Void(Ada-Ada).42

Figure 4. Ada-Ada unit and its void.



Ada-Dia.129 (Ada=30) Dia.29 (Ada=4) Filled-void(Ada-Ada).71 (Ada=20=(4×6)/2+4+4)

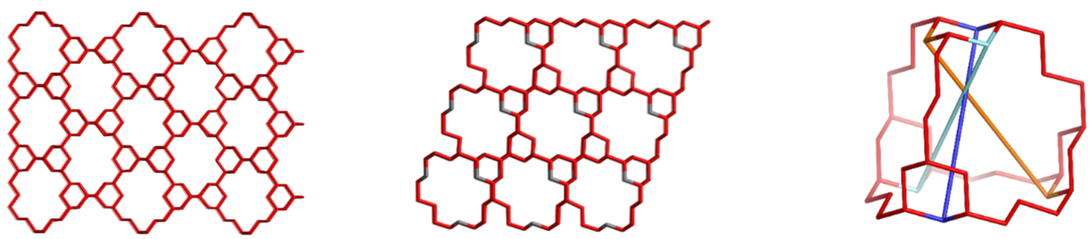
Figure 5. Ada-Ada unit and its void (filled by Dia net; Ada=no. adamantane units).



Ada-Dia embedding   Dia.29 defects in Dia net   Ada-Ada net (empty of Dia.29)

Figure 6. Ada−Ada / Dia net embedding.

Any crystal net has its co-net, the complementary net; of course, the two nets are one and the same, only the building blocks, can be distinctly designed (see Figure 4, left and right). Translating Ada-Ada.100 (Figure 4, left) along the orthogonal coordinates, results in the Ada-Ada net (Figure 6, right); from this structure, one may cut-off the corresponding Ada-Ada co-net (ortho, Figure 7, left); the translation failed in case of the complementary tile, the void(Ada-Ada).42 (Figure 4, right), however, it was successful if translated this void by inclined (60^o) coordinates [17] (Figure 7, middle and right).



Ada-Ada co-net (ortho)   Ada-Ada co-net (inclined)   Void-42_inclined (60^o)

Figure 7. Ada−Ada co-net.

The Ada-Ada binodal net (and its co-net) is characterized by the vertex connectivity (LC) and vertex ring surrounding (LR) sequences, as shown in Table 1; LC is the layer matrix of connectivity [18-20] while LR is the corresponding matrix of rings around each vertex in the graph [21]. The characterization of crystal networks by rings, was used in crystallographic characterization as the vertex symbol vs; however, only in the Topo Group Cluj papers a sequence of all rings surrounding (coming from the layer matrix of rings, of which entries are the sum of all rings around, of the choice length) was described [7, 22].

2.2. OMEGA POLYNOMIAL CHARACTERIZATION OF [3]HHCH(6) AND ADA−ADA NETWORKS

Omega polynomial $\Omega(x)$ is defined on the ground of opposite edge strips *ops* in the graph [23-25] Denoting by *m*, the number of *ops* of length $s=|S|$, one can write: $\Omega(x) = \Sigma_s m_s x^s$. Its first derivative (in $x = 1$) can be taken as a graph invariant or a topological index: $\Omega'(1) =$

$\Sigma_s\, sm_s = |E(G)|$. The CI (Cluj-Ilmenau) index [26] is calculated from $\Omega(x)$ (in $x = 1$) as: CI = Ω'^2-(Ω'+ Ω'').

Table 1. Ada-Ada binodal net characterization: connectivity (LC) and atom ring surrounding (LR).

Tile: Ada-Ada.100; (deg=4(40); deg=2(60); R_6=40; R_8=30; R_{18}=4)		
Atom type	LC	LR
deg=4; vs. $6^3.8^3.18^6$	4. 6. 9. 15. 18. 27. 45. 54. 75. 105	12. 30. 54. 90. 108. 162. 270. 324. 486. 738. 756
deg=2; vs. $6^2.8^2.18^2$	2. 6. 8. 9. 18. 24. 30. 54. 70. 74	6. 24. 48. 60. 102. 144. 180. 324. 432. 528. 780

There are graphs with single *ops*, which is a Hamiltonian circuit. For such graphs, Omega polynomial has a single term: $\Omega(x) = 1x^{s}$; $s = |E(G)|$; it is the case of rhombellanes, as defined in the introductory part of this paper.

For the rod-like network [n]HHCH, the Omega polynomial and CI-index are as follows

$$\Omega(x) = 6x + nx^6 + x^{6(n+1)} \;;\quad CI = 108(n+1)^2 - 36(n+1) + 30$$

In case of Ada-Ada 3D-network, the Omega polynomial is more complicate:

$$\Omega(x) = \sum_{i=1}^{n-1} 8x^{i(2n+1)} + 4x^{n(2n+1)} + x^{12n(4n^2+5n+1)}$$

The above results were obtained by numerical analysis of series of structures with increasing number of building blocks.

Table 2. Omega polynomial in [n]HHCH and Ada-Ada polymers (examples).

n	HHCH		Ada-Ada
	Polynomial	CI	Polynomial
1	$6x^1+1x^6+1x^{12}$	390	$4x^3+1x^{120}$
2	$6x^1+2x^6+1x^{18}$	894	$8x^5+4x^{10}+1x^{648}$
3	$6x^1+3x^6+x^{24}$	1614	$8x^7+8x^{14}+4x^{21}+1x^{1872}$
4	$6x^1+4x^6+1x^{30}$	2550	$8x^9+8x^{18}+8x^{27}+4x^{36}+1x^{4080}$
5	$6x^1+5x^6+1x^{36}$	3702	$8x^{11}+8x^{22}+8x^{33}+8x^{44}+4x^{55}+1x^{7560}$

Structures and data were performed by the Nano-Studio software program [27] developed at Topo Group Cluj.

3. CONCLUSION

Rhombellanes are mathematical structures existing in various environments, in crystal or quasicrystal networks, or even in their homeomorphs, the lasts providing a plethora of molecular graphs, finally candidates to the status of real molecules [see also 28−30].

Rhombellanes originate in the $K_{2.3}$ complete bipartite graph, found as a motif in the linear polymeric staffanes. In close analogy, and using the cube-rhombellane structure, the rod-like (yet hypothetical) polymer [n]HHCH was designed, with vertices of connectivity 6 coming from the hexahydroxy-cyclohexane, HHCH. Further, the idea of linear polymer synthesized from dehydro-adamantane, DHAda, was extended in the design of a three-dimensional crystal network, called here Ada-Ada, of which tile/building block is a hyper-adamantane (an adamantane of which vertices are just adamantanes). It was suggested that Ada-Ada would be synthesized starting from the real molecule tetrabromo-adamantane, by dehydrogenation and polymerization. The crystal structures herein proposed were characterized by connectivity and ring sequences and also by the Omega polynomial, also used in defining the rhombellane structure. It is strongly believed that Mathematical Chemistry can approach to the real needs of Chemistry by studies as that herein presented.

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