Geometry optimization of nC_{24} cyclic polyyne cluster

Lorentz JÄNTSCHI

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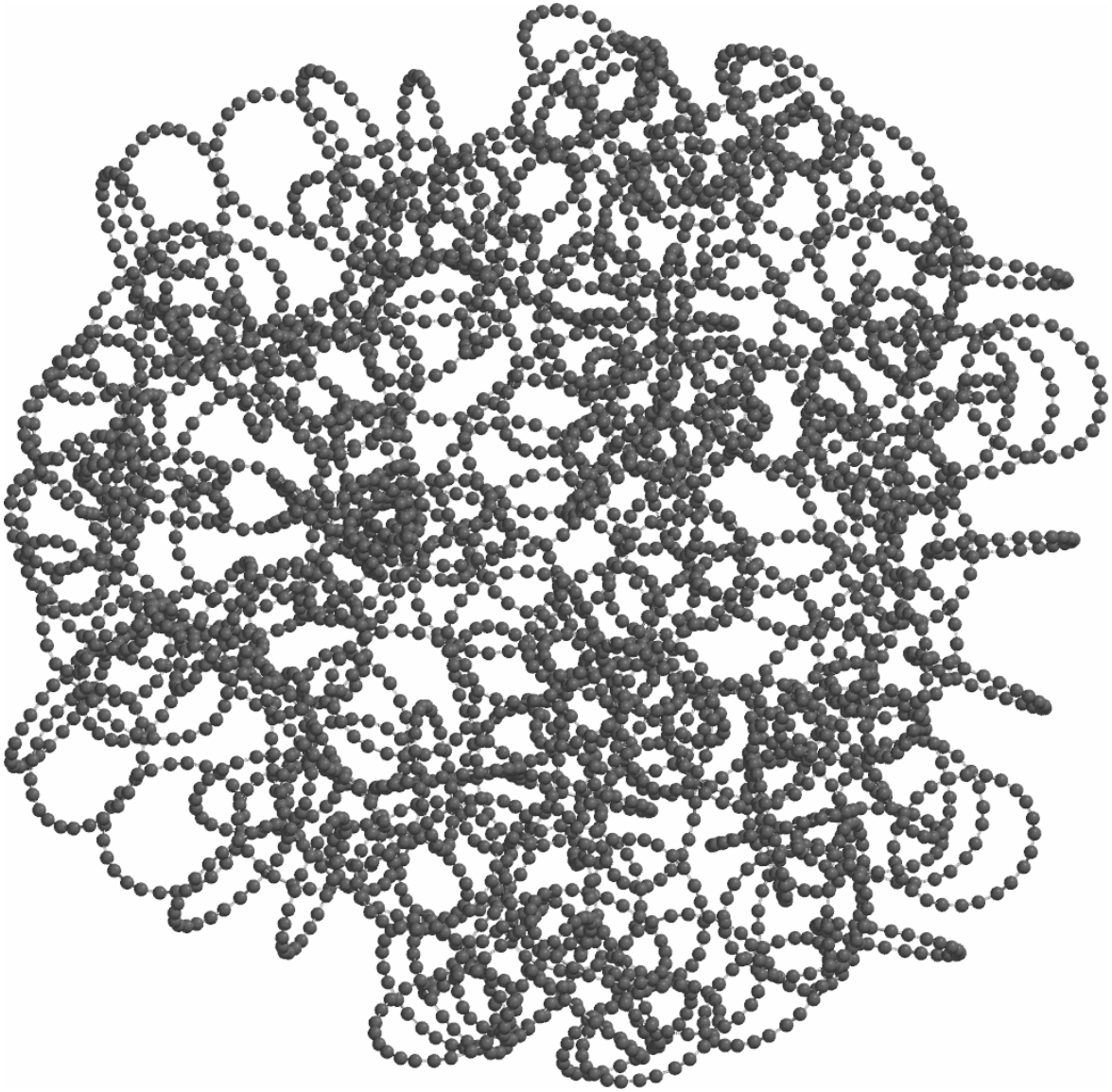
$190C_{24}$ (4560 Carbon atoms)



Outline

- Background
- Motivation
- Aim
- Material
- Method and algorithm
- Identified sub-problems
- Program and results
- Conclusion

Background (1/2)

- Polyyne is a carbon allotrope obtained from alternating single and triple bonds between carbon atoms. Polyynes were first synthesized before 1900 year by oxidative dimerization of phenylacetylides. Both theoretical (Karpfen, 1979; Fan & Pfeiffer, 1989) and experimental (Akagi et al., 1987) studies were dedicated to date to investigate this polymer.
- Evidence that crosslinking the chains of polyyne stabilizes the cluster were found previously (Springborg & Kavan, 1992 &1993). The tendency of the polyynes to form rings was observed at laser vaporization of graphite as secondary product in the synthesis of fullerenes (Hunter et. al., 1993), when the observed rings ranged from C_{22} to C_{46}.
- Cyclic polyynes is a particular subject of interest since it possesses a high order of symmetry.
- Some studies reports special mechanical properties of the condensed polyyne bulks (Itzhaki et al., 2005; Pour et al., 2006; Zhang et al., 2011).
- Despite of the previous beliefs that C_n polyyne is more stable for $n = 4 \cdot k + 2$ (e.g. n = 6, 10, 14, 18, 22, 26, etc.) than for $n = 4 \cdot k$ (e.g. n = 4, 8, 12, 16, 20, **24**, etc.) platinum capped chains of C_n polyynes with n = 20, 24 and 28 were obtained (Zheng & Gladysz, 2005) with very good yields (72%, 36% and 51% respectively).

Background (2/2)

- Inspired by the enabling of simple methods of preparation (Inoue et al., 2010) as well as of their stabilization by cyclization - as were seen as byproduct in the synthesis of fullerenes (Hunter et al., 1993), a study were conducted in order to determine the optimal value of the n for which C_n to be a stable cyclic polyyne, susceptible to conjugation and were found to be 24 (Jäntschi et al., 2016).
- In (Jäntschi et al., 2016) previous study were investigated the optimal size of polyynes to form rings were investigated also the formation of a cluster of 4 crossing C_{24} cyclic polyynes.
- The stability of the cyclic polyynes is expected to increase with the degree of interaction, e.g. via Van der Walls forces, and therefore here the formation and conformation of C_{24} cyclic polyyne bigger clusters obtained by crossing each polyyne with other three was subjected to investigation.

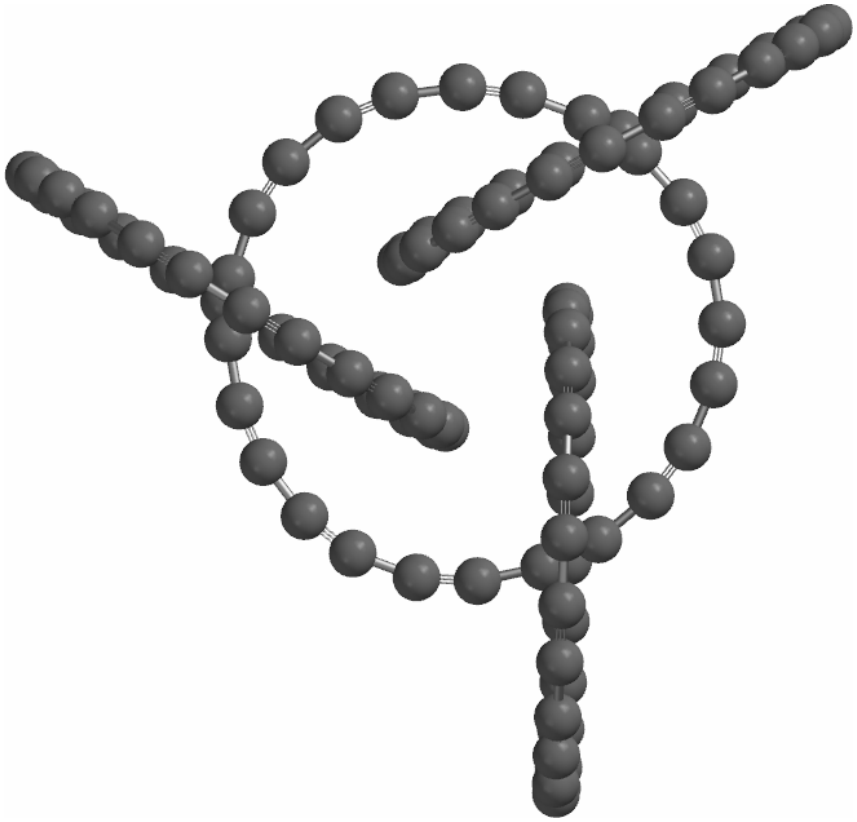
Motivation

- Geometry optimization of molecular clusters is slightly different than the geometry optimization of molecules since at clusters the degrees of freedom no longer represents the atoms positions itself but the molecules positions.
- Also with the increasing of the number of atoms, any software doing blind energy minimization of the cluster the optimization time increases exponentially.
- Even building of a molecular cluster is a challenge for molecular modeling software.

Aim

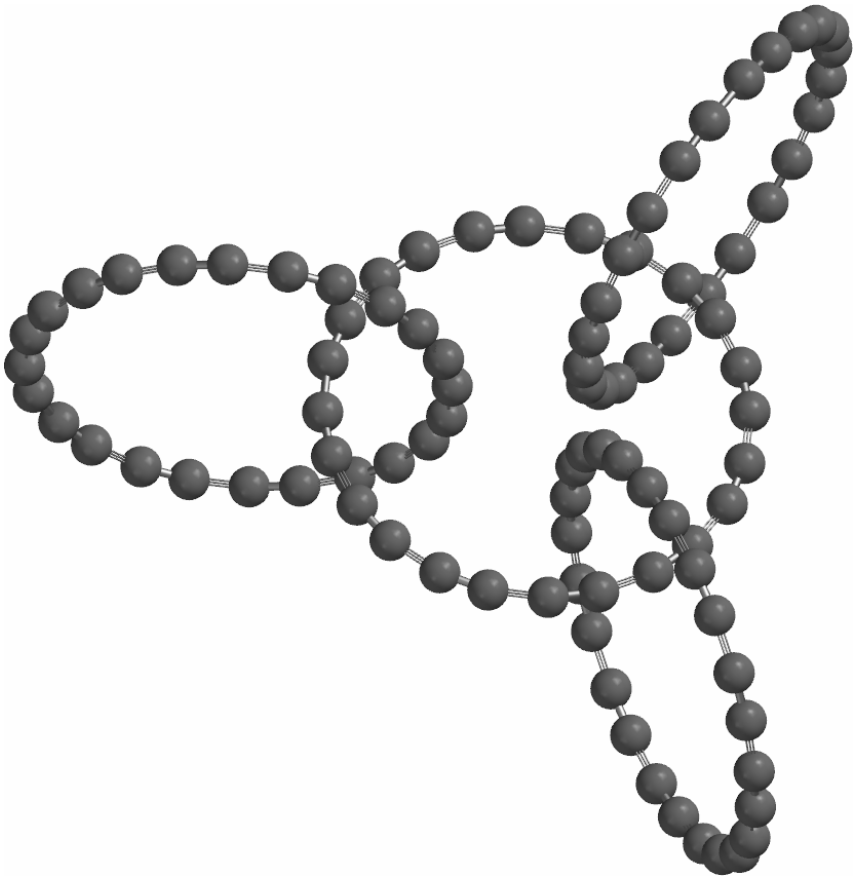
- Here are reported a study regarding the developing of an geometry optimization (energy minimization) program at molecular mechanics theory level designed to provide a good profile for the conformation of crossed nC_{24} polyynes by the pattern previously found - each cyclic polyyne is crossed by another 3.

Pattern



Previously reported (&true only for $4C_{24}$)

(conformer #0)



Used in this study (nC24, &true also for $4C_{24}$)

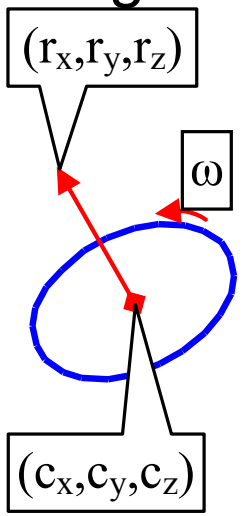
(conformer #1)

Material

- Clusters of $10C_{24}$ (240 Carbon atoms) & $22C_{24}$ (528 Carbon atoms) were designed by the pattern by involving successive geometrical 3D rotations and translations and replications of the C24 cyclic polyyne as well as of its cluster.
- The resulted clusters was subjected to energy minimization (geometry optimization) with Spartan'14 @ HF/STO-G theory level.
- As expected, the computational time was huge.
- As result, and a program was developed to do a 'pre-optimization' at 'molecular mechanics' (or maybe less) theory level.

Method & algorithm (1/2)

- Several tricks were found and implemented during the algorithm & program development.
- Finally (in the final version of the program):
  - a molecule (C_{24}) position was characterized 7 d.f.:
    - its center (three Cartesian coordinates);
    - its 'direction' (three angular coordinates);
    - its 'inside' rotation;
  - The molecule itself is characterized by:
    - its radius;
    - the 'at center' angles corresponding to the lengths of the triple and single bonds



- Thus, the subject of optimization was $7 \cdot n$ variables corresponding to the degrees of freedom of the molecules positions in the nC_{24} cluster.
- The optimization involved iterative changing of the values of the variables (variables $\leftrightarrow$ degrees of freedom).

Method & algorithm (2/2)

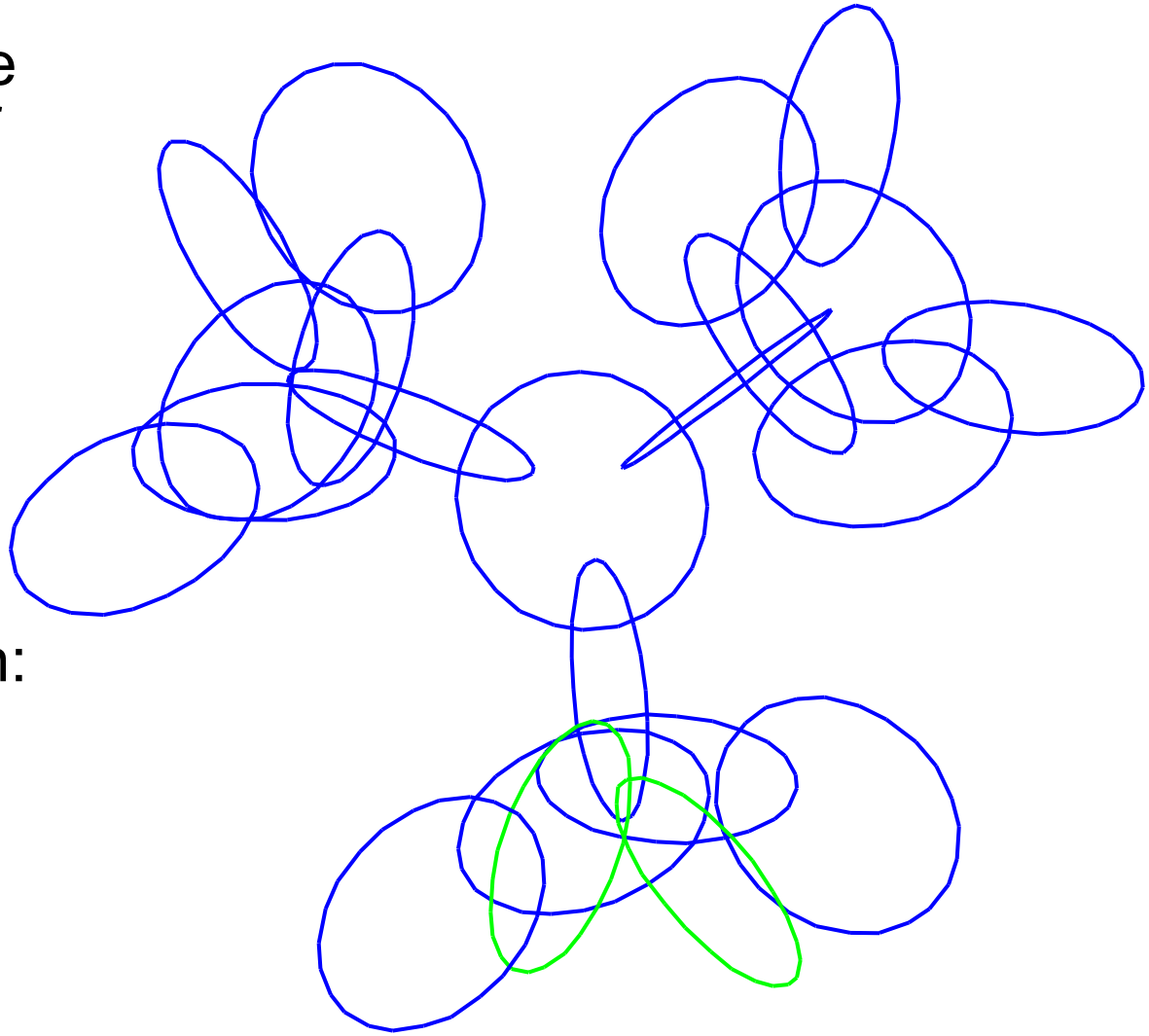
- Since all atoms are Carbon, and all atoms have the same constrains (a single and a triple bond) supplementary coefficients or constants other than the distance parameterizing interaction were not necessary. The optimization score which was found to be suitable is the sum of the inverses of the fourth power of the distance between atoms, consistent with the hard nuclear forces interacting between atoms. Optimization objective corresponding to the optimization objective is to minimum.
- Other trick is how to keep the molecules together since the tendency of the optimization score is to depart the molecules one to any other.

Doing of symmetry operations

- For cluster growing ($4C_{24} \rightarrow 10C_{24} \rightarrow \ldots$)
- For cluster optimization
- For cluster symmetry annalysis
- Operations:
  - 3D rotation by an referential axis (Ox, Oy, Oz)
  - 3D rotation fitting a given direction
  - 3D translations
  - 3D rotation by an arbitrary axis

Crosses analysis

- At beginning (of the optimization and of the grow): identifying the crosses

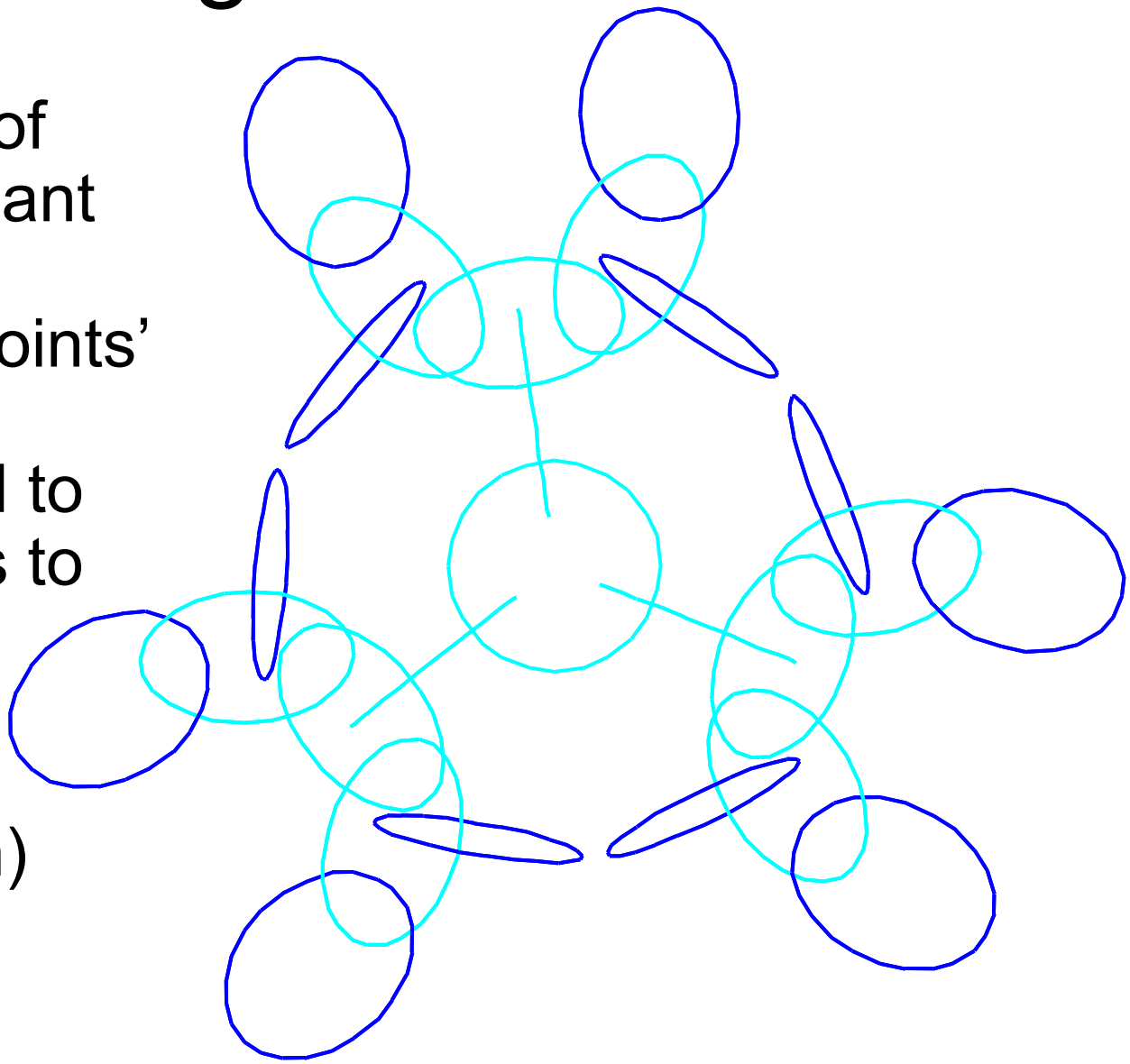


- During optimization: testing a cross

- Alignment (rotation & translation) were involved

Growing a cluster

- A succession of operations meant to identify the ‘intervention points’ – outer rim molecules and to add molecules to the cluster (rotations and translations involved again)



Program & results

- A FreePascal program was developed and parameterized correspondingly to be used for any value of the n to do the geometrical optimization of the nC_{24} cluster. Program has been tested for $4C_{24}$, $10C_{24}$, $22C_{24}$, $46C_{24}$, and $94C_{24}$ and it works.
- In order to keep the molecules together, the module identifying the crosses was used as constrain during the optimization.
- The crosses of each molecule to another are actually the second topology level of the cluster, if the bonds between the atoms are considered to be the first.
- Further, a special limitative growing case were identified, optimized and analyzed – $28C_{24}$.
- From solution proposed by the developed program, HF/STO-G optimization were conducted and Spartan'14 fastly minimized the cluster energy (optimum found after 52 cycles).

Program interface

```
Running "d:\polyyne\polyynes_analyze\v_sym_4\clusterx.exe "
Subject file: p6
Job to to (1-6):
1: Reindex mols from center to outer rim.
2: Calculate distance paths for outer rim.
3: Generate next bigger cluster.
4: Optimize cluster.
5: Build molecule of centers.
6: Symmetry analysis.
3
hin/p6 cluster read HIN completed.
Coordinates & versors calculated.
Centers reset to the 1st molecule.
Versors reset to the z axis aligned by the 1st molecule.
Angles aligned.
Crosses identified.

46<-45; 47<-45; 48<-44; 49<-44; 50<-43; 51<-43; 52<-42; 53<
37; 63<-37; 64<-36; 65<-36; 66<-35; 67<-35; 68<-34; 69<-34;
79<-29; 80<-28; 81<-28; 82<-27; 83<-27; 84<-26; 85<-26; 86<
n/p6_next.hin hin/p6_next.log) saved to disk.
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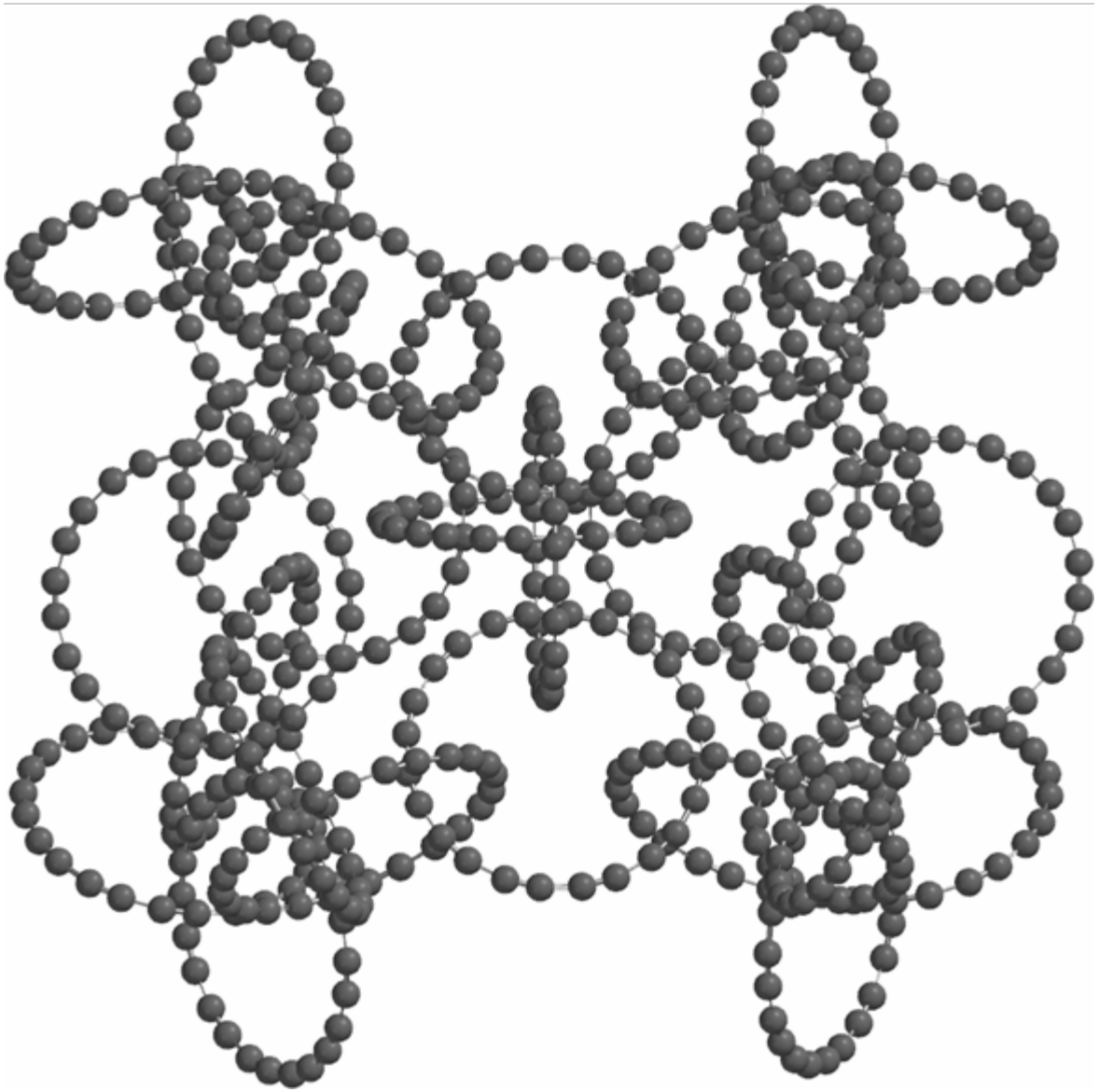
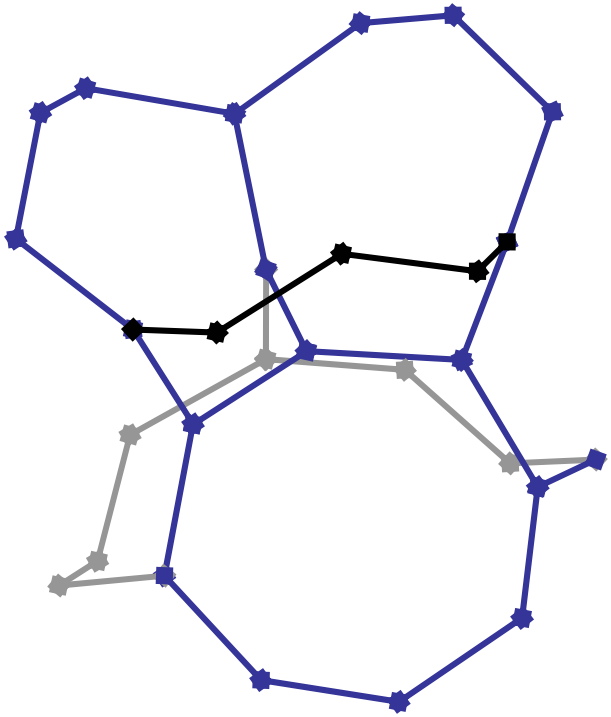
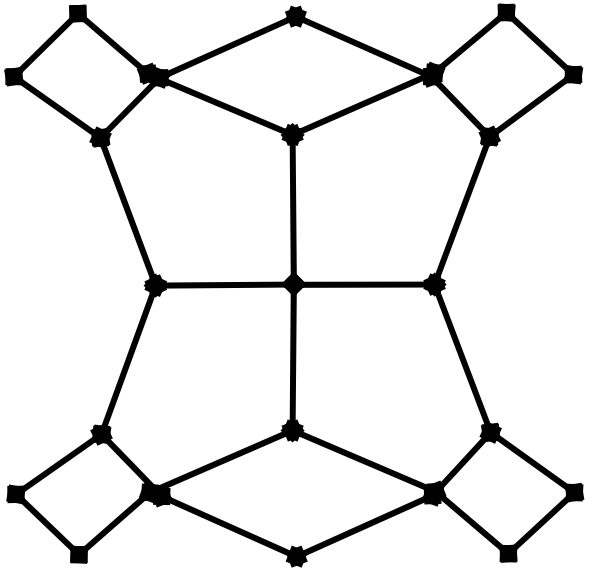
$28C_{24}$ atoms (672)



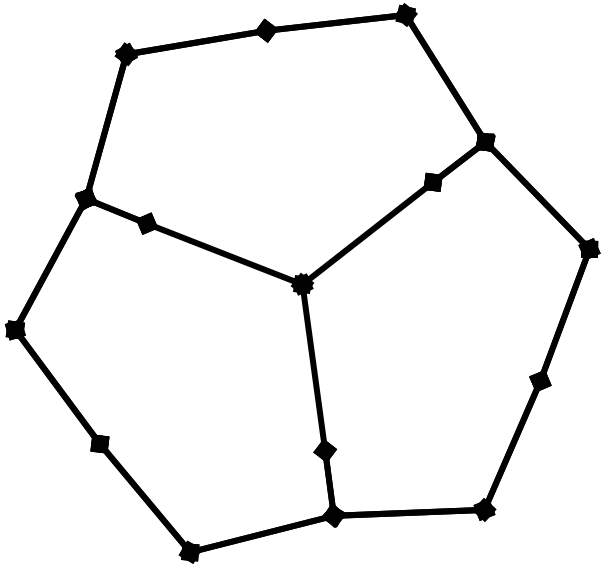
$28C_{24}$ centers topology (D_{3h})



Perspective view



Side view (C_2 side)



Side view (C_3 side)

Conclusion

- The study revealed that the developed program performs very well in the optimization of the geometry of the cluster and can be used as a first approximation before modeling at (Post-)Hartree-Fock theory levels.

References

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