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FULL PAPER

Conformational study of C_{24} cyclic polyyne clusters

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Abstract

Polyynes were first synthesized before the year 1900, and isolated and characterized after 2000. Cyclic polyynes are of particular interest since possess a high order of symmetry. Furthermore, some studies reported special mechanical properties of the condensed polyyne bulks. The optimal size of polyynes to form rings has been previously investigated and was found to be 24 with a stable cluster of crossing four C_{24} cyclic polyynes. We investigated in this study the conformation of clusters of polyynes (nC_{24}) by the pattern previously identified to stabilize the cluster. Clusters of $4C_{24}$, $10C_{24}$, $22C_{24}$, $46C_{24}$, and $94C_{24}$ were designed and subjected to energy minimization. The main finding is the preservation of the symmetry for the nC_{24} cluster with the increase of its size. The study revealed that $4C_{24}$, $10C_{24}$, and $22C_{24}$ preserve a high symmetry and the calculations suggest an excellent increasing of the cluster stability with the increase of the number of polyyne rings. A $22C_{24}$ derived cluster namely $28C_{24}$ was found as the one likely to limit the growth of the polyyne clusters.

KEYWORDS

cluster modeling, cluster properties, cyclic polyynes, energy minimization, geometry optimization, symmetry analysis

1 | INTRODUCTION

Polyyne is a carbon allotrope obtained from alternating single and triple bonds between carbon atoms. Both theoretical[1,2] and experimental[3] studies were used to investigate this polymer. Evidence that crosslinking the chains of polyyne stabilizes the cluster were reported in the scientific literature.[4,5] The tendency of the polyynes to form rings was observed at laser vaporization of graphite as a secondary product in the synthesis of fullerenes,[6] with rings ranged from C_{22} to C_{46}. C_n polyyne was found 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.). However, platinum capped chains of C_n polyynes with $n = 20$, 24, and 28 were obtained with very good yields (72%, 36%, and 51%, respectively).[7]

Polyynes have important properties such as hardness,[8] and auxeticity (capacity to become thicker when stretched and thinner when compressed),[9] being known as strong and electronic material with very high mobility.[10] Different methods such as acetylene coupling approach, or liquid-phase laser ablation have been used in the synthesis of chain polyynes.[11] Furthermore, the stabilization of the polyynes by cyclization was used in the synthesis of fullerenes.[6] A previous study was conducted to determine the optimal value of the n for which C_n become a stable cyclic polyyne, susceptible to conjugation, and proved equal to 24.[12] The stability of the cyclic polyynes is expected to increase with the degree of interaction, for example, via Van der Waals forces. Therefore, the conformation of C_{24} cyclic polyyne clusters obtained by crossing each polyyne with other three was subjected to the investigation in this study.

2 | METHODS

The C_{24} molecule (Figure 1A) and $4C_{24}$ (Figure 1B) cluster reported previously[12] were used as the starting point in this research.

The external rings of the $4C_{24}$ cluster were crossed with other two polyynes ($10C_{24}$ in Figure 1C). The resulted structure was optimized at different Hartree–Fock (HF) and post-Hartree–Fock theory levels (methods: HF STO-G,[13–16] 3-21G,[17] 6-31G*,[18] M06,[19] DFT,[20]

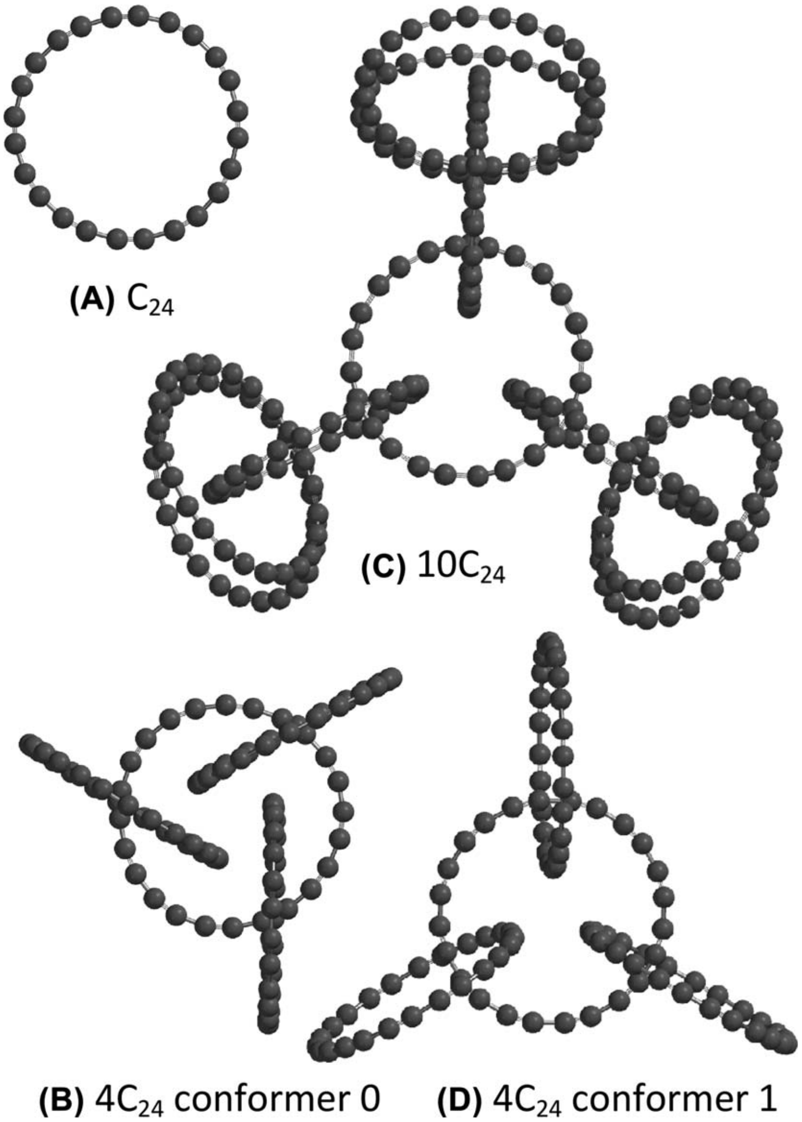

FIGURE 1 C_{24} cyclic polyyne crossing clusters formation

B3LYP,[21] 6-31G*, MP2[22,23]) since the previous finding revealed two $4C_{24}$ conformers, the second conformer being identified after optimization (Figure 1D).

The optimized conformation of $4C_{24}$ from Figure 1D along with the optimized conformation of $10C_{24}$ in Figure 1C provided results (see Table 1) useful for further design of the nC_{24} clusters congeners ($n = 4, 10, 22, 28, 46, 94$).

In all optimized conformations, the molecule was found not close enough to the plane. One expectancy is to have the atoms positioned alternatively in two parallel plans, but also this scenario is subjected to be lucky in the optimization process since many meta-stable pseudo-conformations for C_{24} exist. Even more, the geometry is subject to small changes when other C_{24} polyynes cross the C_{24} molecule subjected to the analysis. Therefore, a regular approximation for the C_{24} conformation was taken to build the nC_{24} cluster—an icositetragon (reasoning R1 in Table 1) circumscribed to a circle. The value of the molecule radius is an average of the distances of the atoms relative to the center of the mass of the molecule, and the planarity of the molecule is an idealization (reasoning R2 in Table 1). The triple and single bonds alternate in the C_{24} molecule, and, therefore, the icositetragon have edges alternating in length (corresponding to the single and the triple bond). Therefore, each length can be expressed in angular units relative to the mass center of the molecule (reasoning R3 and R4 in Table 1). It must be noted that also the used values represents rounded values and $12\cdot(13.75°+16.25°) = 360°$.

In regards of the crossed molecules, each molecule crosses another molecule at an approximate perpendicular position (reasoning R5 in Table 1), and all three crossing molecules have an angle around 120° one to each other (reasoning R6 in Table 1).

TABLE 1 Information used to the design nC_{24} clusters

Subject	Information (u)	Value	Reasoning[a]
C_{24} molecule	shape	icositetragon	R1
	radius (Å)	4.96[b]	R2
	C≡C bond (°)	13.75	R3
	C—C bond (°)	16.25	R4
two crossed C_{24}	angle between (°)	90	R5
two C_{24} crossing the same C_{24}	angle between (°)	120	R6

u = units of measurements;
[a] See the text;
[b] Full number implemented in the program was 4.9554426 Å.

3 | ALGORITHM AND SOFTWARE IMPLEMENTATION

Our hypothesis was that the design given by the rules obtained after geometry optimization for C_{24}, $4C_{24}$, and $10C_{24}$ and presented in Table 1 is optimal and fit to the construction of nC_{24} clusters.

The nC_{24} (n = 4, 10, 22, 46, 94, and 28) clusters were constructed and their geometries were optimized. On one hand, it may seem simple to build the nC_{24} clusters, but to do this by hand is at least adventurous (for instance, $46C_{24}$ have 1104 carbon atoms). On the other hand, none of the available software is able to minimize the energy of molecular clusters, because optimizing the geometry of a cluster is a different approach than optimizing the geometry of a single molecule. The classical optimization with Spartan'14 software running on a 16-core-based machine (with a max. of eight cores/task limitation—software limitation) showed unsatisfactory results. The optimization is too preoccupied by the conformation of the molecules itself (the atoms are more close by each other, so, Hessian updates are based on these changes) rather than the optimization of the arrangement of the molecules in the cluster. The optimization at the HF level are very costly in terms of computing time when actually is a matter of moving molecules as groups. The semiempirical and molecular mechanics approaches do their job but break the symmetry of the molecules far ahead of finishing their jobs, which becomes unsuitable for our study.

Therefore, two problems need solutions: how to generate a bigger cluster starting from a previous one (e.g., $4C_{24}$ from C_{24}, $10C_{24}$ from $4C_{24}$, etc.), and how to optimize the geometry of this cluster.

The findings given in Table 1 allow an iterative construction of the next bigger cluster, but still involve a series of approaches related, for example, with rotations, translations, adds, and reverting to initial perspectives.

For the second problem, namely the optimization of the cluster, a proper approach needs to be found. One job is to do an "energy minimization" or "geometry optimization" at atomic level and another thing is to do the same at molecular level, in such a way that the molecules to became frozen during the process. A full geometry minimization taking into account the atomic level too can be involved, trying to make adjustments at relative positions of atoms in molecules and having as effect small changes, not far away by the expected (or educated guess) equilibrium. Our solution to this problem is presented in this manuscript.

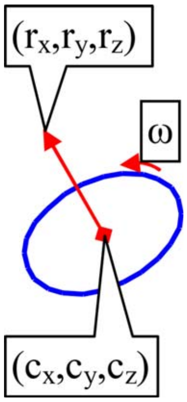

FIGURE 2 Degrees of freedom of a C_{24} molecule in nC_{24} cluster

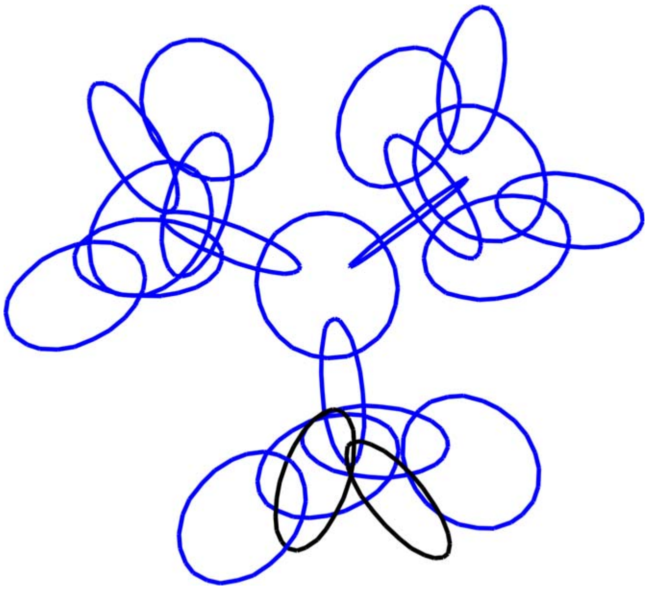

FIGURE 3 Testing a cross between two molecules

3.1 | Movement of a molecule

Each molecule in the cluster has 7 degrees of freedom. The degrees of freedom (df) can be conveniently assigned (Figure 2) to the center of the molecule (3 df), the direction of the plane containing the molecule (3 df), and to the angular rotation of the molecule (or, more explicit, of its first atom or first bond on the perimeter of the circle circumscribing the molecule, 1 df).

3.2 | Interaction between molecules

Atoms of a molecule act attractive and repulsive forces that are in equilibrium, keeping the atoms together with all atomic valences satisfied. Interactions between molecules also exist, but mainly steric effects drive the arrangement. Since all atoms have fulfilled their need for electrons, few cohesion forces are keeping close the molecules.

On one hand, the repulsive forces drive away the molecules and the general tendency is to occupy as largest space as possible. Different approaches were tested to minimize the sum of the inverses of the *k*th power (from $k = 2$) of the distance between atoms (Equation 1).

$$\sum_{i}\sum_{j} 1/(\mathrm{dist}(\mathrm{atom}_i, \mathrm{atom}_j))^k \tag{1}$$

where $1 \le i < n_{\mathrm{atoms}}$ and $i < j \le n_{\mathrm{atoms}}$, $k \ge 2$, the sums correspond to each pair of atoms taken once.

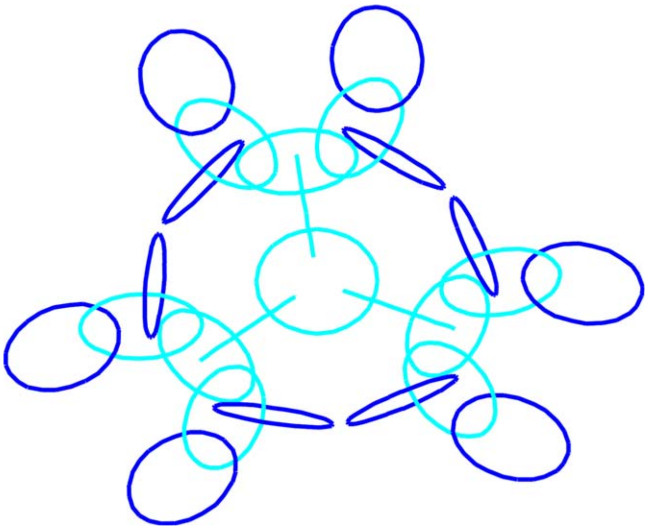

FIGURE 4 Adding molecules to the outer rim

TABLE 2 Designed nC_{24} clusters

Stage	Cluster	Crossed C_{24} Triple-	Single	Molecules	Atoms
1	C_{24}	0	1	1	24
2	$4C_{24}$	1	3	4	72
3	$10C_{24}$	4	6	10	240
4	$22C_{24}$	10	12	22	528
5	$46C_{24}$	22	24	46	1104
6	$94C_{24}$	46	48	94	2256
4*	$28C_{24}$	10	0	28	336

The testing was stopped when the value of k showed an evolution of the conformation going in an expected way (a clear tendency of the molecules to occupy the free space between them).

Minimizing the sum of the inverses of the fourth power ($k = 4$) of the distances between atoms (Equation 1) was found to be suitable for solving the problem. When $k = 4$, the highest penalization is on the smallest distances, so when two atoms from two different molecules are too close by each other is reflected as the most substantial quantity which drives the direction of the changes in the positions.

Since geometry optimization of the cluster is not about changing relative position of the atoms inside one molecule, but about changing the relative positions of the molecules inside the cluster, the geometry optimization of the cluster turned to be a problem with $7\cdot(m - 1)$ degrees of freedom, where m is the number of molecules in the cluster. Furthermore, the Equation 1 was simplified in terms of computation, to include only pairs of atoms from different molecules, as given in Equation 2:

$$\sum_{i}\sum_{j}\sum_{u=1}^{24}\sum_{v=1}^{24} 1/(\mathrm{dist}(\mathrm{atom}_{i,u},\mathrm{atom}_{j,v}))^{4} \tag{2}$$

where $1 \le i < n_{\mathrm{mols}}$ and $i < j \le n_{\mathrm{mols}}$.

In the Equation 2, the first two sums correspond to each pair of C_{24} molecules taken once, and the last two sums are for all atoms in the pair of molecules.

On the other hand, the molecules are relatively free to move, but once a cross is formed, it cannot be broken unless one of the molecules is broken. Therefore, when a change appears in the cluster, is required to know if the change has driven away a molecule cross. Thus, a new problem appeared, namely testing a cross (Figure 3).

Crosses analysis is involved at the formation of the cluster when the crosses are identified as well as during the optimization of the cluster when a change to a molecule is subject to test if does not change its crosses. To test a cross, rotations and translations are applied to align the molecules by the axis of coordinates.

3.3 | Outer rim

When a cluster is grown, the external polyynes, the ones placed in the outer rim and having exactly one cross with other molecules, are subject to the addition of crosses with two new molecules (Figure 4).

FIGURE 5 Cyclic polyyne $10C_{24}$ clusters

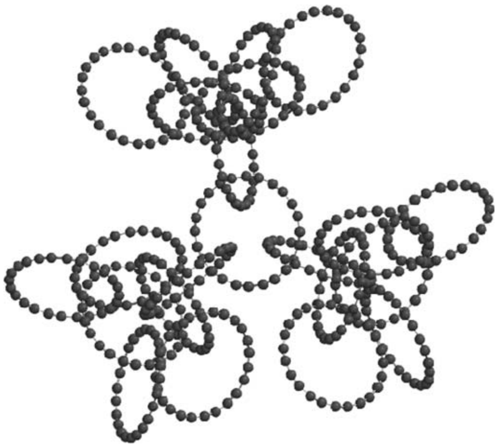

FIGURE 6 Cyclic polyyne $22C_{24}$ cluster

The simplest way to add two new molecules crossing a molecule from the outer rim (Figure 4) is (1) to align the molecule by rotations and translations in the center of the coordinate system, (2) to rotate it such that the molecule which already crosses it to be on a plane of coordinates (such as yOz), (3) to add the new molecules as indicated by Table 1, and (4) to revert the new cluster at the initial positions.

3.4 | Implementation

A routine was designed to generate the nC_{24} clusters and another one to optimize the geometry of the clusters. The routines were implemented in FreePascal[24] working with nonparallelized code (no parallelization was possible for the optimization). The program is available on request from the authors.

The following approaches were implemented in the programs:

- Geometrical manipulation of the molecules—rotations, translations, and alignment;
- Construction of the skeleton molecule to be added in the process of building the cluster;
- Translation from and to atoms coordinates versus degrees of freedom: molecule center (3 df), molecule direction (versor, 3 df), and relative position of the first (or any other) atom (circle's rotation in its plane, 1 df)—see Figure 2;
- Calculation of the optimization objective (sum given in Equation 2 of repulsive forces to min.);
- Identification and test for the crosses—see Figure 3;
- Adding molecules to the outer rim—see Figure 4;

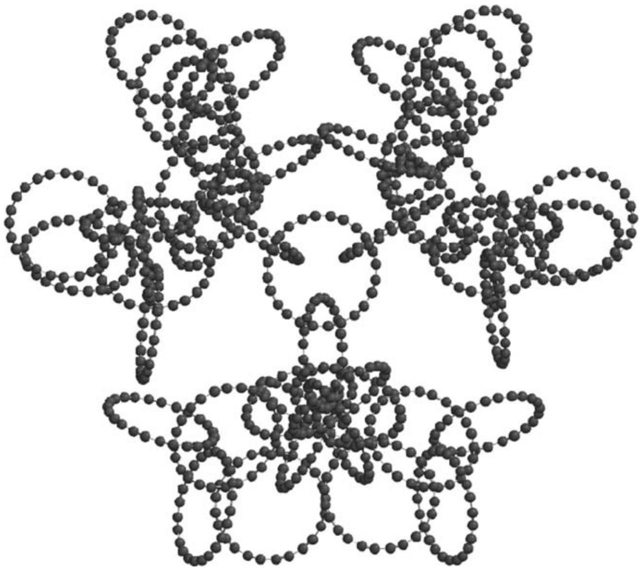

FIGURE 7 Cyclic polyyne $46C_{24}$ cluster

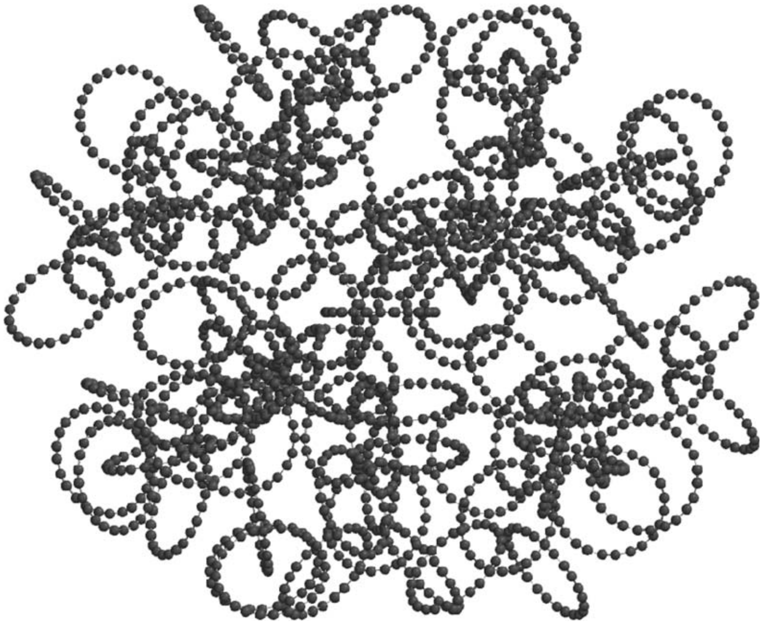

FIGURE 8 Cyclic polyyne $94C_{24}$ cluster

- Generating the centers of the molecule—if the molecule is the first level of topology, by connecting the atoms together, then the cluster is the second level of topology, connecting the molecules together. If a molecule is replaced by its center, and each cross by a connection, then the first level of topology disappears and the second level of topology become the first (and a new molecule is obtained, the "molecule of centers");
- Symmetry analysis—identification of the center of symmetry, and of the first and second axis of symmetry. Two symmetry orders were calculated: one taking into account the positions of the atoms and the second considering only the positions of the molecules (symmetry for the molecule of centers).

4 | RESULTS AND DISCUSSION

The implemented methodology successfully obtained the nC_{24} clusters. The characteristics of the obtained clusters are presented in Table 2.

One outer rim of molecules was subjected to addition of two new crossing molecules from one stage to another. The images of the obtained clusters are given in Figures 5–9.

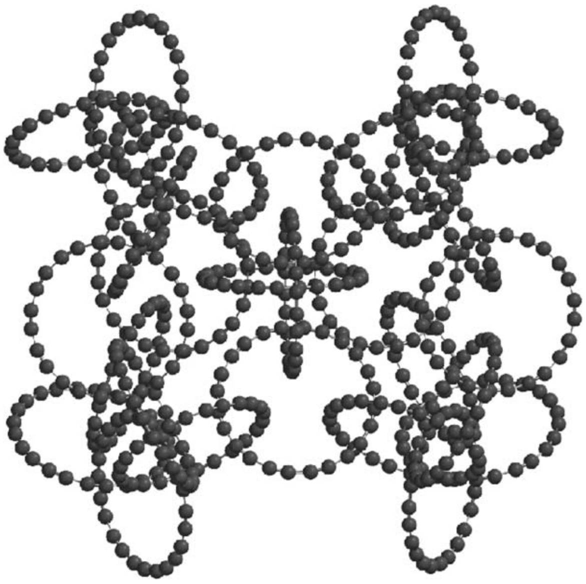

FIGURE 9 Cyclic polyyne $28C_{24}$ cluster

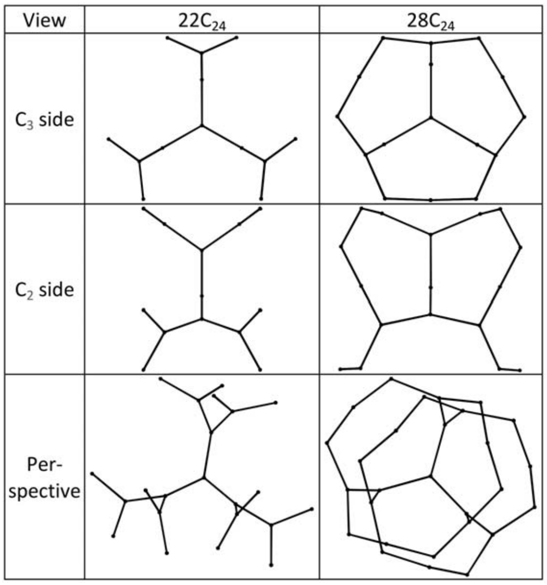

FIGURE 10 Geometrical conformation of the molecular centers of coordinates for cyclic polyyne $22C_{24}$ and $28C_{24}$ (symmetry: D_{3h})

It should be noted that small changes in the angles between molecules appear, and these changes increase with the growth of the cluster from $10C_{24}$ (Figure 5) to $94C_{24}$ (Figure 8).

The molecule of the centers, the virtual molecule obtained by placing an atom in the position of the center of each molecule and using a bond to link these new atoms, for $22C_{24}$ (Figure 6) and $28C_{24}$ (Figure 9) clusters is depicted in Figure 10.

Figure 10 shows the topological level of the cluster that was kept frozen during the optimization, allowing the preservation of topology and the optimization of geometry. A little change in the angles between molecules appears when the $28C_{24}$ cluster is formed from the $22C_{24}$ cluster (see Figure 10). The difference between $22C_{24}$ and $28C_{24}$ is visible at the *C_3 side* only at outer rim, the angles between the molecules in this rim in $28C_{24}$ are not at 120°, two of them became closer to 90° to accommodate the presence of another one (3 visible, other three overlapped, visible only in the *Perspective view*) connecting them. Furthermore, at the *C_2 side*, small changes in the conformation are also seen, also at the outer rim. At this level, the changes are propagated back to the whole cluster until its inner rim, and *C_2 side* reveals these changes. It is visible how perfect 120° angles in the *Perspective* of $22C_{24}$ at the level of the inner rim are changed too in $28C_{24}$.

From the solution proposed by the developed program, HF/STO-G optimization was conducted for $22C_{24}$ and $28C_{24}$ and Spartan'14 minimized the cluster energy. The optimum was found after 52 cycles for $28C_{24}$ and after 234 cycles for $22C_{24}$. The energies (in Hartrees) from the optimization are given in Table 3.

The supplementary cross produced by the six molecules added to the $22C_{24}$ cluster decreased the total energy per molecule in an insignificant quantity (less than 0.02 Hartrees per molecule, see Table 3). It can be say based on this result that $22C_{24}$ and $28C_{24}$ are with the same stability.

The symmetry analysis, conducted on the clusters both at the atomic and molecular level (on the molecule of centers), provided important information regarding the growth of the nC_{24} cyclic polyyne clusters (Table 4).

The analysis of the results presented in Table 4 reveals that the high order of symmetry (D_{3h}) is preserved until $28C_{24}$ and both clusters presented in Figure 10 possess the same high order of symmetry (see Table 4).

It is an explanation for the growing process; it is a little more expensive in the space than the available space surrounding the cluster. Therefore, with the increasing of the size of the cluster, the unused space is consumed and somewhere around $22C_{24}$ (which includes $28C_{24}$, because $28C_{24}$ is actually a $22C_{24}$ with other six molecules bridges between the branches of the cluster), this unused space is consumed. For the next growths ($46C_{24}$ and $94C_{24}$), the growth of the cluster is realized with costs on the steric effect, and this is why the symmetry is completely lost.

TABLE 3 Total energy of clusters (from HF/STO-G theory level)

Cluster	Energy (Hartrees)	Energy per molecule (Hartrees)
$22C_{24}$	−19 729.19	−896.78
$28C_{24}$	−25 109.43	−896.77

TABLE 4 Symmetry orders of the clusters

Cluster	Symmetry order Atomic level	Molecular level
$4C_{24}$	C_S	D_{3h}
$10C_{24}$	C_S	D_{3h}
$22C_{24}$	C_{3h}	D_{3h}
$28C_{24}$	C_{3h}	D_{3h}
$46C_{24}$	C_1	C_1
$94C_{24}$	C_1	C_1

4.1 | Approach suitability

The presented approach is limited to the investigations with the same constrains as those presented in this manuscript. The inverse of fourth power works nicely only when the same type of atoms are in the molecule. Unexpected results may appear when other atoms are involved, and this is tackled by MMFF94 molecular mechanics approach that uses a database of known measurements for the distances between atoms as recipes on the way of the optimization process. Other methods, such as semi-empirical, HF, and post-HF methods act similarly. For instance, in the HF and post-HF, the same is implemented at the level of shielding constants from Gaussian integrals (measurements → Slater-type orbital → Gaussian-type orbital).

The used of crossed molecules in the cluster is another constraint of the presented approach. Without crossing, any trial to optimize may diverge (for instance it may work too if one molecule is trapped inside of another molecule) because does not use a valley shape function (such as the dependence of the energy at the formation of the H_2 molecule from atoms). In this case, it just merely tries to accommodate the molecules in the space by maximizing the small spaces on the cost of larger ones (if it is available space at infinity, then the optimization goes there).

Nevertheless, the extension of our approach may have success when the distances between molecules (or between the atoms of different molecules) are much larger than the distances between the atoms. This change in the expression of the objective function due to the presence of different atoms should be negligible compared with the ideal case when it is included. Furthermore, this method does not intend to provide the optimized cluster, it intends to provide only a much better starting point for modeling using superior theory levels approaches. Some examples of calculations starting with the optimized clusters are provided in Table 5.

No other molecular clusters were investigated with the proposed procedure. The limitations related to the investigation of other molecular clusters should be mainly regarding the possibility of relative movement of the molecules in the cluster. If the molecules in the cluster are free to move apart from the cluster in the initial conformation, then constrains needs to be added to the objective function of the optimization to assure a valid function. In the presented case, we used the natural constraint (namely, the crossed molecules are not allowed to break apart). A procedure check at each stage of the iteration if the initial topology of the cluster is preserved, and the change is made only if this is true. The same principle may work in any other case of cluster optimization if the constraints are identified and implemented in the program.

TABLE 5 Properties calculations by example

Cluster	MMFF94[a] Solvation energy	PM6[a] Heat of formation (kJ/mol)	MM+[b] Energy (kCal/mol)	OPLS[b] Energy (kCal/mol)
$4C_{24}$	−330.22	12 229.65	1479.10	326.75
$10C_{24}$	−815.73	30 677.57	3709.38	839.54
$22C_{24}$	−1784.02	67 602.89	8175.67	1874.92
$28C_{24}$	−2243.83	[c]	10 399.11	2365.76
$46C_{24}$	−3715.66	[d]	17 128.33	3390.73
$94C_{24}$	−7567.98	[d]	35 102.69	8407.03

[a] Spartan software.
[b] Hyperchem software.
[c] Too many CC triple bonds.
[d] Too many atoms (max = 900, here ≥ 920).

5 | CONCLUSIONS

The developed program for molecular clusters energy minimization performs well in the optimization of the geometry of clusters (works perfectly on $n\mathrm{C}_{24}$ cyclic polyynes clusters) and can be used as a first approximation before modeling at (Post-)Hartree–Fock theory levels (shortening the computational time).

$28\mathrm{C}_{24}$ is a special limiting growth case of the $n\mathrm{C}_{24}$ cluster with high symmetry (D_{3h}; $22\mathrm{C}_{24}$ have 24 positions open for growing, $28\mathrm{C}_{24}$ have 18, while $46\mathrm{C}_{24}$ have 24) with 6 outer rim crosses which stabilizes further the conformation of the cluster. It is very likely that either $22\mathrm{C}_{24}$ or $28\mathrm{C}_{24}$ are the most probable representatives of the $n\mathrm{C}_{24}$ stable cyclic polyyne clusters.

The treatise of the cluster as the second level of the molecular topology when the molecule is seen as being the first opens a new simplified way to analyze large molecular ensembles and it can be very useful especially in finding their conformation.

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