

# Chapter 23

## Cyclic Carbon Polyynes

Lorentz Jäntschi, Sorana D. Bolboacă, and Dusanka Janezic

**Abstract** Monocyclic rings with even carbon atoms, from 6 to 24, were studied using five restricted Hartree–Fock computational refinements (STO-3G, 3-21G, 6-31G\*, RI-MP2/6-31G\*, and RI-MP2/6-311G\*) in order to identify stable polyyne rings. Polyynes with 24 carbon atoms were revealed to be stable, and a crossed cyclic polyynane, with 4 such rings, was designed in order to evaluate its condensed state stability. Density functional theory calculation was performed on this nanostructure. The study predicted stable monocyclic polyynane for a number of C atoms equal or higher than 16. The distance between carbon atoms followed an exponential decay to a limit value very near to the distance in  $C_{24}$  polyynane, sustaining its stability. The condensed  $4C_{24}$  polyynane seemed to be stable, with a sum of bond order per atom of 3.78. The total energy value calculation leads to the conclusion that condensation by crossing the rings failed to provide supplementary stabilization, but also did not induce destabilization. The theoretical IR spectrum as well as

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L. Jäntschi

Department of Physics and Chemistry, Technical University of Cluj-Napoca, Muncii Blvd.  
no. 103-105, RO-400641 Cluj-Napoca, Romania

Institute for Doctoral Studies, Babeş-Bolyai University, Kogălniceanu Street no. 1, RO-400084  
Cluj-Napoca, Romania

University of Agricultural Science and Veterinary Medicine Cluj-Napoca, Calea Mănăştur  
no. 3-5, RO-400372 Cluj-Napoca, Romania

Department of Chemistry, University of Oradea, Universităţii Street no. 1, RO-410087 Oradea,  
Romania

e-mail: [lorentz.jantschi@gmail.com](mailto:lorentz.jantschi@gmail.com)

S.D. Bolboacă (✉)

University of Agricultural Science and Veterinary Medicine Cluj-Napoca, Calea Mănăştur  
no. 3-5, RO-400372 Cluj-Napoca, Romania

Department of Medical Informatics and Biostatistics, Iuliu Haţieganu University of Medicine  
and Pharmacy, 6 Louis Pasteur, 400349 Cluj-Napoca, Romania

e-mail: [sbolboaca@umfcluj.ro](mailto:sbolboaca@umfcluj.ro)

D. Janezic

Natural Sciences and Information Technologies, Faculty of Mathematics, University of  
Primorska, SI-6000 Koper, Slovenia

e-mail: [dusanka.janezic@gmail.com](mailto:dusanka.janezic@gmail.com)

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the thermodynamic parameters of  $4C_{24}$  polyynes was rationalized from a molecular dynamics study.

### 23.1 Background Information on Polyynes

Polyynes are the oligomeric cousins of carbene, having linear chains of sp-hybridized carbon atoms (Smith and Buseck 1982) that are of scientific interest either as linear or cyclic complexes (McCarthy et al. 2000). Carbon, a chemical element with three naturally occurring isotopes ( $^{12}C$  and  $^{13}C$ , stable, and  $^{14}C$ , radioactive), is part of several compounds, such as those summarized in Fig. 23.1.

Polyynes, organic compounds with alternating single and triple bonds ( $-C\equiv C-$ )<sub>n</sub> (where  $n > 1$ ), have been reported in the scientific literature since 1951 (Bohlmann 1951a, b, c; 1955). Significant contributions to the chemistry of naturally occurring acetylenes are attributed to Bohlmann (1951a, b, c, 1953, 1955; Bohlmann et al. 1955, 1962) and Jones (2003). Synthetic routes to hydrogen terminated linear polyynes have been reported since 1972 (Eastmond et al. 1972).

Polyynes have been the focus of much study because of their unique feature, the carbon-carbon triple bonds (Cataldo 2006). A chain with over 300 carbons and alternating triple and single bonds was reported in 1995 by Lagow et al. (1995). Such linear alternating chain has been demonstrated to possess the properties of both metals and semiconductors (Gorjizadeh et al. 2011) and behave like electronic materials with very high mobility (Zhang et al. 2011).

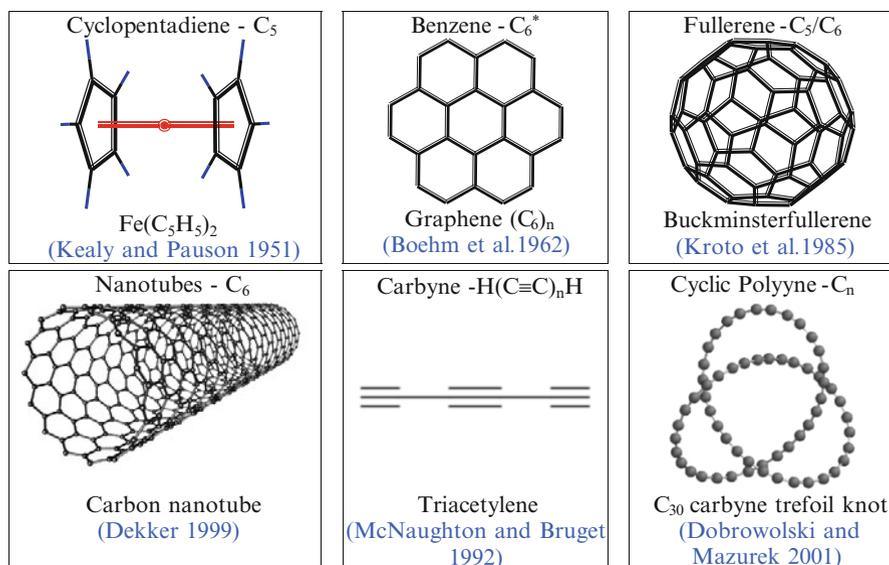


Fig. 23.1 Carbon-based compounds

Cyclic polyynes, in particular the acetylene-based polymers, have also been investigated. Examples of these include the cyclic  $C_{10}$ ,  $C_{14}$ , and  $C_{18}$  polyynes (Anderson 2012) or the  $C_6$ – $C_{26}$  clusters (Li 2012), which are all-carbon structures. Information regarding the stability of polyyne rings is essential in identification of new materials with interesting properties.

The present study reports a computational chemistry study of cyclic polyynes at the post-Hartree–Fock (HF) level of theory in order to rationalize the stabilization of polyyne rings in a condensed arrangement.

## 23.2 Monocyclic Polyynes

The cyclic polyynes with an even number of carbon atoms, from 6 to 24, were investigated. The following approach has been applied in characterization of monocyclic ring polyynes:

- Geometry optimization: The structural optimization of the investigated structures was performed by Spartan (v. 10, <http://www.wavefun.com>) ab initio package at the restricted (post)-HF (Hartree–Fock) (Hartree 1928a, b; Fock 1930a, b; Hartree and Hartree 1935) level of theory. Five computational refinements were explored: STO-3G (slater-type orbitals – Gaussian approximated with  $5 \cdot n$  basis functions (Hehre et al. 1969)), 3-21G (with  $9 \cdot n$  basis functions (Moller and Plesset 1934)), 6-31G\* (split-valence basis sets with  $15 \cdot n$  basis functions (Ditchfield et al. 1971)), RI-MP2/6-31G\* (with  $15 \cdot n$  basis functions, MP = Møller–Plesset perturbation method (Moller and Plesset 1934), 2 = second order, RI = resolution of the identity), and RI-MP2/6-311G\* (with  $18 \cdot n$  basis functions). In all cases,  $n$  is the number of carbon atoms.
- Rationalization: To characterize the monocyclic ring polyynes, the average energy per atom and distances between C atoms have been calculated under the investigated refinements of theory levels.

### 23.2.1 Energy Assessment

Stable monocyclic ring of polyynes was calculated beginning with six carbon atoms – the first even number investigated. The energy values obtained for monocyclic polyynes are listed in Table 23.1.

As can be observed from Table 23.1, the energy values decrease as the number of C atoms in the monocyclic ring increases. This decrease is steep until  $n = 14$ , and

**Table 23.1** Average energy per atom (E(kcal/mol)) for a single monocyclic ring polyynes, calculated at different theory levels

<i>n</i>	STO-3G	3-21G	6-31G*	RI-MP2/6-31G*	RI-MP2/6-311G*
6	$-37.308 \cdot n$	$-37.577 \cdot n$	<sup>a</sup>		
8	$-37.329 \cdot n$	$-37.593 \cdot n$	<sup>a</sup>		
10	$-37.346 \cdot n$	$-37.610 \cdot n$	<sup>a</sup>		
12	$-37.352 \cdot n$	$-37.614 \cdot n$	<sup>a</sup>		
14	$-37.358 \cdot n$	$-37.619 \cdot n$	$-37.829 \cdot n$	<sup>b</sup>	
16	$-37.361 \cdot n$	$-37.621 \cdot n$	$-37.831 \cdot n$	$-37.958 \cdot n$	$-37.970 \cdot n$
18	$-37.363 \cdot n$	$-37.624 \cdot n$	$-37.833 \cdot n$	<sup>c</sup>	
20	$-37.364 \cdot n$	$-37.625 \cdot n$	$-37.835 \cdot n$	$-37.961 \cdot n$	$-37.973 \cdot n$
22	$-37.365 \cdot n$	$-37.626 \cdot n$	$-37.836 \cdot n$	<sup>c</sup>	
24	$-37.366 \cdot n$	$-37.627 \cdot n$	$-37.836 \cdot n$	$-37.962 \cdot n$	$-37.974 \cdot n$

*n*, number of carbon atoms (only the coefficients were included in the exponential fit)

<sup>a</sup>symmetry broken at 6-31G\* level of theory

<sup>b</sup>planarity broken at RI-MP2/6-31G\* level of theory

<sup>c</sup>optimization oscillated between equilibrium states

then it becomes and remains very slight. The exponential fit reveals a decay that supports the stabilization of the monocyclic rings at C<sub>23</sub>. For STO-3G level of theory, the fit is

$$\hat{Y} = -37.3664 + 0.2482 \cdot \exp(-n/4.1462)$$

$$R^2 = 0.9977; R^2_{\text{adj}} = 0.9970; F = 1494$$

where  $\hat{Y}$  = energy per atom estimated by the exponential function, *n* = number of C atoms in the monocyclic ring,  $R^2$  = determination coefficient,  $R^2_{\text{adj}}$  = adjusted determination coefficient, and *F* = Fisher's statistics associated with the regression model.

The minimum energy values were in every case related to the STO-3G basis set, while the maximum values were provided by RI-MP2/6-311G\* whenever it could be calculated, depending upon the stability of the monocyclic ring polyynes (see Table 23.1). The following interesting observation about the stability of monocyclic ring polyynes could be made: stabilization of the polyynes occurs when the number of carbon atoms is a multiple of 4 and no less than 16. As can be concluded from the exponential decay of the average energy per C atom, starting with *n* = 16, the cyclic polyynes quickly approach the minimum energy state. The difference due to RI-MP2/6-311G\* in the average energy values per atom for polyynes between C<sub>20</sub> and C<sub>24</sub> is less than 1% · *n*.

### 23.2.2 Bond Length

The stability of a monocyclic ring can be assessed by inspection of the C–C and C≡C interatomic separation, i.e., the bond lengths (Table 23.2). Analysis of the results presented in Table 23.2 shows:

- In general, there is a decrease in C≡C length, when  $n$  increases, for STO-G, 3-21G, and 6-31G\* levels of theory; there are two exceptions (at C<sub>14</sub> and C<sub>18</sub>) for 3-21G and one exception (at C<sub>18</sub>) for 6-31G\*.
- The general trend is a smooth increase in the C≡C bond length and a smooth decrease of C–C length for the RI-MP2/6-31G\* and RI-MP2/6-311G\* levels of theory; the C–C length increases systematically in the monocyclic rings, and those differing by four C atoms are clustered with a smooth decrease at C<sub>22</sub> and C<sub>24</sub> for STO-G level of theory; the C–C distance systematically increases in the monocyclic rings, and those differing by four C atoms are clustered with a plateau as the difference between C<sub>18</sub> and C<sub>22</sub> is concerned for 3-21G level of theory.

The plot of C≡C bond lengths, provided by STO-3G (column 2, STO-3G/d<sub>1</sub> in Table 23.2), vs. the number of atoms ( $n$ ) also shows an exponential decay which fits well with the observed values while (C≡C;C<sub>24</sub>) is near to the estimated optimal value of 118.63 pm:

$$\hat{d}_{\text{STO-3G}}(\text{C}\equiv\text{C}; \text{C}_n) = 118.63(\pm 0.27) + 152(\pm 54) \cdot e^{-n/2.3(\pm 0.3)}$$

The above equation estimates a value of 119.6 pm for  $n = 12$  while the calculated value is of 119.0 pm, a value of 118.7 pm for  $n = 18$  while the calculated value is of 118.6 pm, and a value of 118.6 pm for  $n = 24$  while the calculated value is of 118.6 pm.

**Table 23.2** C≡C and C–C bond length in monocyclic rings at different theory levels

$n$	STO-3G		3-21G		6-31G*		RI-MP2/6-31G*		RI-MP2/6-311G*	
	C≡C	C–C	C≡C	C–C	C≡C	C–C	C≡C	C–C	C≡C	C–C
6	129.8	129.8	129.5	129.6	<sup>a</sup>					
8	123.7	142.1	123.3	139.5	<sup>a</sup>					
10	120.4	138.9	122.1	133.8	<sup>a</sup>					
12	119.0	141.4	119.7	138.3	<sup>a</sup>					
14	119.2	139.9	120.3	135.9	121.7	136.0	<sup>b</sup>			
16	118.8	140.3	119.7	137.0	119.7	138.5	125.2	135.7	125.0	135.4
18	118.8	139.9	119.9	136.2	119.8	138.0	<sup>c</sup>			
20	118.7	139.9	119.7	136.5	119.6	138.1	125.5	134.6	125.3	134.3
22	118.7	139.8	119.7	136.2	119.6	137.9	<sup>c</sup>			
24	118.6	139.8	119.6	136.2	119.6	138.0	125.7	133.9	125.6	133.6

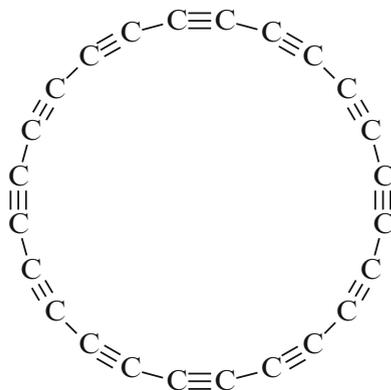
$n$ , number of C atoms in monocyclic polyyne ring, bond length in pm

<sup>a</sup>symmetry broken at 6-31G\* level of theory

<sup>b</sup>planarity broken at RI-MP2/6-31G\* level of theory

<sup>c</sup>optimization oscillated between equilibrium states

**Fig. 23.2** C<sub>24</sub> standard chemical structure



### 23.2.3 Stable Monocyclic Polyynes

The monocyclic ring with 24 atoms appeared to be a stable complex, and subsequent work was performed on the polycyclic C<sub>24</sub> polyynes (Fig. 23.2).

The crossed arrangement of the polyynes was of interest in this study and was driven at 6-31G\* level of refinement for geometry optimization. A stable C<sub>24</sub> cyclic polyynes in a form of crossed cycles was searched.

### 23.2.4 Characteristic Polynomials of C<sub>24</sub> Polyynes

The characteristic polynomial (noted here with  $P_\varphi$ ), calculated by the determinant of the matrix obtained as a difference between unity matrix  $I_{|V|}$  multiplied with a symbolic variable ( $X$ , for instance) and the adjacency matrix ( $Ad$ ),

$$P_\varphi(X) = P_\varphi(X, G) = |X \cdot I_{|V|} - Ad(G)|$$

has been evaluated for C<sub>24</sub> polyynes.

Characteristic polynomial, as other polynomials, encodes the topological information of a chemical structure and can be seen as a source of structural descriptors used in structure–property/activity modeling (Ivanciuc et al. 1999; Balasubramanian and Randi 1982; Jäntschi et al. 2009; Bolboacă and Jäntschi 2007).

The characteristic polynomial was computed in two different ways: the classical characteristic polynomial (ChP) and a weighted polynomial. For this, the adjacency matrix (“0/1,” Table 23.3) was replaced by the bond order matrix (“0/1/3”; see Table 23.4).

The characteristic polynomial ChP of C<sub>24</sub> polyynes is

**Table 23.3** C<sub>24</sub> polyyne: negative signed adjacency matrix

[Ch]	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
1		-1	0	0	0	-1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
2	-1		0	0	0	0	0	0	-1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
3	0	0		-1	0	0	0	-1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
4	0	0	-1		-1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
5	0	0	0	-1		-1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
6	-1	0	0	0	-1		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
7	0	0	0	0	0	0		-1	0	0	0	-1	0	0	0	0	0	0	0	0	0	0	0	0
8	0	0	-1	0	0	0	-1		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
9	0	-1	0	0	0	0	0	0		-1	0	0	0	0	0	0	0	0	0	0	0	0	0	0
10	0	0	0	0	0	0	0	0	-1		0	0	-1	0	0	0	0	0	0	0	0	0	0	0
11	0	0	0	0	0	0	0	0	0	0		-1	0	0	0	-1	0	0	0	0	0	0	0	0
12	0	0	0	0	0	0	-1	0	0	0	-1		0	0	0	0	0	0	0	0	0	0	0	0
13	0	0	0	0	0	0	0	0	-1	0	0	0		-1	0	0	0	0	0	0	0	0	0	0
14	0	0	0	0	0	0	0	0	0	0	0	0	-1		0	0	-1	0	0	0	0	0	0	0
15	0	0	0	0	0	0	0	0	0	0	0	0	0	0		-1	0	0	0	-1	0	0	0	0
16	0	0	0	0	0	0	0	0	0	0	-1	0	0	0	-1		0	0	0	0	0	0	0	0
17	0	0	0	0	0	0	0	0	0	0	0	0	0	-1	0	0		-1	0	0	0	0	0	0
18	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-1		0	0	-1	0	0	0
19	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0		-1	0	0	0	-1
20	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-1	0	0	0	-1		0	0	0	0
21	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-1	0	0		-1	0	0
22	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0		-1	0
23	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0		-1
24	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-1	0	0	0	0	

**Table 23.4** C<sub>24</sub> polyyne: negative signed bond order matrix

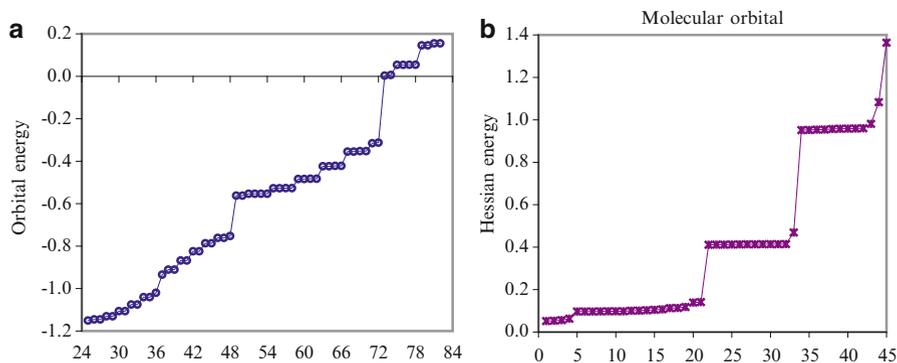
[Ch]	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
1		-3	0	0	0	-1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
2	-3		0	0	0	0	0	0	-1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
3	0	0		-3	0	0	0	-1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
4	0	0	-3		-1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
5	0	0	0	-1		-3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
6	-1	0	0	0	-3		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
7	0	0	0	0	0	0		-3	0	0	0	-1	0	0	0	0	0	0	0	0	0	0	0	0
8	0	0	-1	0	0	0	-3		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
9	0	-1	0	0	0	0	0	0		-3	0	0	0	0	0	0	0	0	0	0	0	0	0	0
10	0	0	0	0	0	0	0	0	-3		0	0	-1	0	0	0	0	0	0	0	0	0	0	0
11	0	0	0	0	0	0	0	0	0	0		-3	0	0	0	-1	0	0	0	0	0	0	0	0
12	0	0	0	0	0	0	-1	0	0	0	-3		0	0	0	0	0	0	0	0	0	0	0	0
13	0	0	0	0	0	0	0	0	0	-1	0	0		-3	0	0	0	0	0	0	0	0	0	0
14	0	0	0	0	0	0	0	0	0	0	0	0	-3		0	0	-1	0	0	0	0	0	0	0
15	0	0	0	0	0	0	0	0	0	0	0	0	0	0		-3	0	0	0	-1	0	0	0	0
16	0	0	0	0	0	0	0	0	0	-1	0	0	0	-3		0	0	0	0	0	0	0	0	0
17	0	0	0	0	0	0	0	0	0	0	0	0	0	-1	0		0	-3	0	0	0	0	0	0
18	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0		-3	0	0	-1	0	0	0
19	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0		-3	0	0	0	0	-1
20	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-1	0	0	0		-3	0	0	0	0
21	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-1	0		0	-3	0	0
22	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0		-3	0	-1
23	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0		-1	-3
24	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-1	0	0	0	0	

$$\begin{aligned} \text{ChP}(\text{C}_{24}\text{polyyne}) = & +1 \cdot x^{24} - 24 \cdot x^{22} + 252 \cdot x^{20} \\ & - 1520 \cdot x^{18} + 5814 \cdot x^{16} - 14688 \cdot x^{14} + 24752 \cdot x^{12} \\ & - 27456 \cdot x^{10} + 19305 \cdot x^8 - 8008 \cdot x^6 + 1716 \cdot x^4 \\ & - 144x^2 \end{aligned}$$

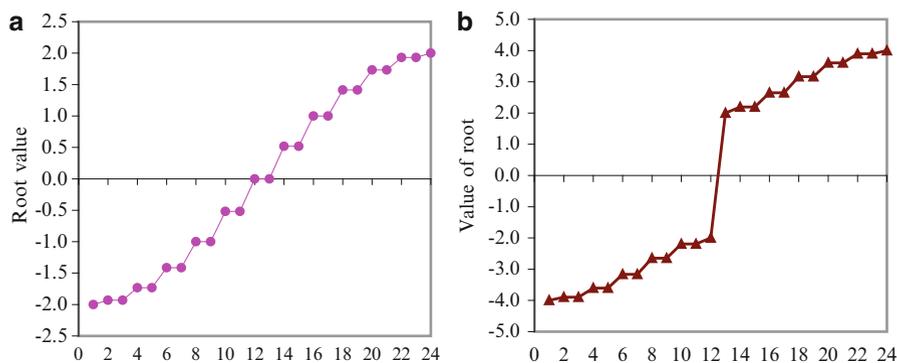
The roots of characteristic polynomial varied from  $-2$  to  $2$ , with an average of  $0$  and a standard deviation of  $1.44$ . The value of Anderson–Darling statistics is equal to  $0.7456$  ( $p=0.4795$  (Jäntschi 2014)) saying that the values of roots are normally distributed.

The orbital energies and the Hessian eigenvalues were furthermore calculated for monocyclic  $\text{C}_{24}$  polyyne. The  $\text{C}_{24}$  polyyne has eighty-two orbitals, ten being unoccupied molecular orbitals (the last ten in the right upper corner of the graph in Fig. 23.3).

The pattern distribution of the characteristic polynomial roots is shown in Fig. 23.4.



**Fig. 23.3** Pattern distribution for monocyclic  $\text{C}_{24}$  polyyne: (a) orbital energy, (b) Hessian energy



**Fig. 23.4** Pattern distribution for monocyclic  $\text{C}_{24}$  polyyne: (a) roots of the characteristic polynomial, (b) roots of the characteristic polynomial on bond order

The coefficient of similarity (Myers 1986) between the root values and values of orbital energy is 43.19 % when 24 roots are compared to 48 orbital energies (the first 24 and the last 10 values not included) and increases to 47.78 % when 24 roots are linked with 24 values of orbital energies. A similar value is found when the similarity of roots and Hessian energy is investigated (42.48 %).

The bond order matrix for monocyclic  $C_{24}$  polyyne is presented in Table 23.4. The pattern distribution of the values of roots of the characteristic polynomial on bond order is presented in Fig. 23.4b.

The coefficient of similarity [29] between values of roots and values of orbital energy is 39.41 % when 24 roots are compared to 48 orbital energies (not included the first 24 and the last 10 values) and increase to 43.59 % when 24 roots are linked with 24 values of orbital energies. A similar value is found when the similarity of roots of the characteristic polynomial on bond order matrix and Hessian energy is investigated (40.74 %).

The characteristic polynomial on bond order ( $ChP_{bo}$ ) of  $C_{24}$  polyyne is

$$\begin{aligned} ChP_{bo}(C_{24}polyyne) = & +1 \cdot x^{24} - 120 \cdot x^{22} + 6492 \cdot x^{20} \\ & - 209200 \cdot x^{18} + 4468374 \cdot x^{16} - 66589920 \cdot x^{14} \\ & + 709365552 \cdot x^{12} - 5438445120 \cdot x^{10} + 29760016905 \cdot x^8 \\ & - 113288996200 \cdot x^6 + 284636017236 \cdot x^4 \\ & - 423644304720 \cdot x^2 + 282428473600 \cdot x^0 \end{aligned}$$

The value of characteristic polynomial on bond order matrix roots varied from  $-4$  to  $4$ , with an average of  $0$  and a standard deviation of  $3.23$ . The value of Anderson–Darling statistics equal to  $1.8896$  ( $p = 0.8936$ ) sustains that the values of roots of characteristic polynomial on bond order matrix are also normally distributed.

### 23.3 Assembly of $C_{24}$ Polyyne

Identification and characterization of condensed cyclic polyynes was done following the next steps:

- Crossing the structures: A trial has been conducted to identify how many monocyclic ring polyyne could be crossed to form a stable crossed structure.
- Geometry optimization: The geometry optimization was conducted on the crossed cyclic polyynes identified at the previous step with the Spartan ab initio package at the restricted (post)-HF level of theory, with 6-31G\* computational refinement. The reason of using 6-31G\* level of refinement could be found in the *Supplementary Material* which shows that for the elements of first period, it is the best choice in estimating the geometry.

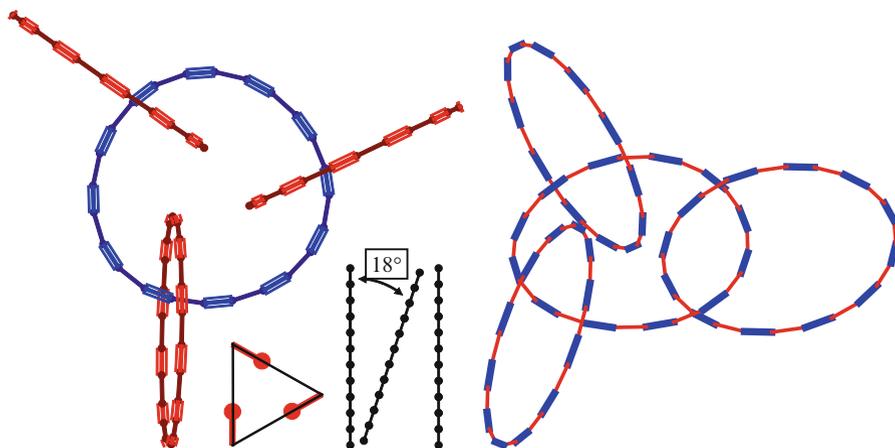


Fig. 23.5  $4C_{24}$  optimized structure of even-C-atom polycyclic cluster at 6-31G\*

- Molecular dynamics study: It has been performed by Spartan using DFT (density functional theory (Pierre and Kohn 1964; Kohn and Sham 1965)) method using M06 functionals (Zhao and Truhlar 2008) at the 6-31G\* basis set.

Geometry optimization revealed that in both the isolated polyynes-24 and the 4-condensed-polyynes-24, the distance between carbon atoms (i.e., the bond length) is optimal (Fig. 23.5):

$$d(C\equiv C) = 120 \text{ pm}, d(C - C) = 136 \text{ pm}$$

The following values were calculated for the  $4C_{24}$  complex (6-31G\* level of refinement): molecular weight = 1153.056 amu, energy = 11785.29 kJ/mol, E-HOMO (energy of highest occupied molecular orbital) =  $-9.36$  eV, E-LUMO (energy of lowest unoccupied molecular orbital) =  $-2.03$  eV, and dipole moment = 0.07 debye.

The molecular dynamics study performed on  $4C_{24}$  using DFT-M06 led to the following reasonable values of thermodynamic parameters: ZPE (zero-point energy) = 1383.93 kJ/mol,  $S$  (entropy) = 1377.75 J/mol,  $H$  (enthalpy) = 5.0861 au (atomic units, 1 au = 2625 kJ/mol),  $G$  (free enthalpy) = 4.9296 au, and  $C_v$  (heat capacity at constant volume) = 1325.31 J/mol.

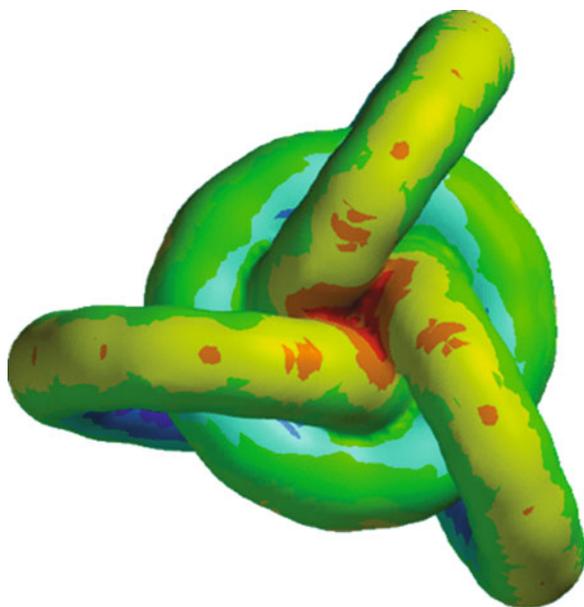
The total energy of the four-cyclic ring structure ( $4C_{24}$ ) was calculated as  $-3587.1360$  kcal/mol, leading to an energy per atom of  $-37.3660$  kcal/at · mol, while the total energy for monocyclic ring  $C_{24}$  was of  $-896.783$  kcal/mol with energy per atom equal to  $-37.3662$  kcal/at · mol. In consequence, condensation of  $4C_{24}$  provided neither supplementary stabilization nor destabilization.

The bond lengths in  $4C_{24}$  optimized structure and the estimated bond orders are listed in Table 23.5.

**Table 23.5** Bond length in  $4C_{24}$  polyyne complex

Ring	Bond	Distance $k \cdot$ distance (pm)	Averaged distance (pm)	Lowden	Mulliken
Belt ring	$C \equiv C$	$11 \cdot 118.8, 1 \cdot 118.7$	$\approx 118.8$	1.16	1.16
Exterior ring #1	$C \equiv C$	$11 \cdot 118.6, 1 \cdot 118.7$	$\approx 118.6$		
Exterior rings #2 and #3	$C \equiv C$	$12 \cdot 118.6$	118.6		
Belt ring	$C-C$	6 (140.2, 140.3)	140.25	2.69	2.70
Exterior rings #1, #2, and #3	$C-C$	$11 \cdot 139.8, 1 \cdot 139.9$	$\approx 139.8$		

$k$  number of bonds

**Fig. 23.6** Electrostatic potential of  $4C_{24}$  polycyclic polyyne

The sum of bond order per atom was of 3.78 (either Lowden or Mulliken) and is near to the ideal value of 4. The average distance between carbon atoms in organic compounds found in literature (Jäntschi 2013) is 154 pm for the  $C-C$  bond, 134 pm for the  $C=C$  bond, and 120 pm for the  $C \equiv C$  bond, while in the proposed polycyclic polyyne, the values were 139.91 pm on average for the  $C-C$  bond and 118.65 pm on average for the  $C \equiv C$  bond. These results obtained on the  $4C_{24}$  condensed cyclic polyyne suggest a high hardness in the solid state.

The electrostatic potential for the proposed polycyclic polyyne is illustrated in Fig. 23.6 and was obtained from the model at DFT-M06 level of theory.

Similar IR spectra were obtained from the molecular dynamics study performed at DFT-M06 theory level on both one monocyclic polyyne (Fig. 23.7) and  $4C_{24}$  polycyclic polyyne (Fig. 23.8). Several similarities could be observed in the

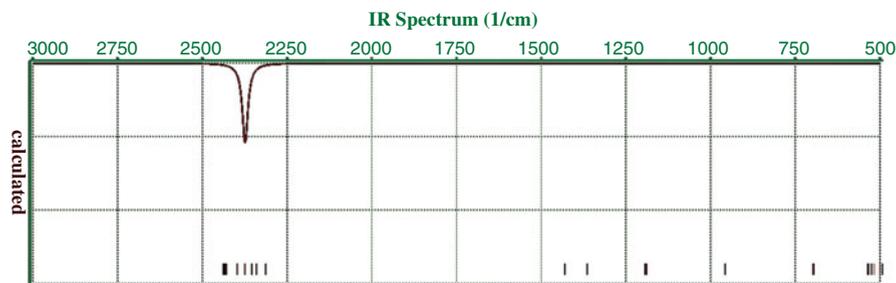


Fig. 23.7 IR spectrum (1/cm) of  $C_{24}$  monocyclic polyynes (at DFT-M06/6-31G\* level of theory)

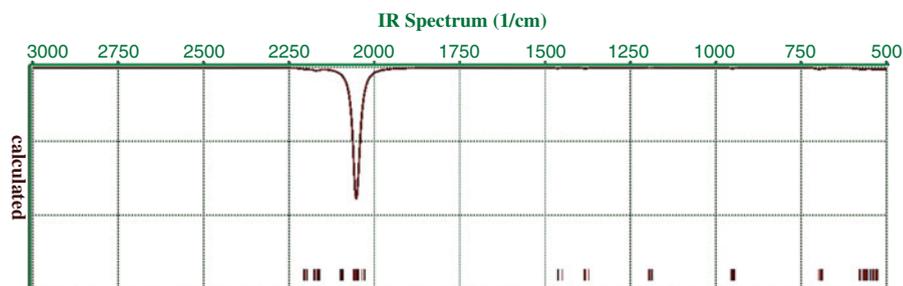


Fig. 23.8 IR spectrum (1/cm) of  $4C_{24}$  polycyclic polyynes (at DFT-M06/6-31G\* level of theory)

obtained IR spectra: there is only one broad band corresponding to the energy absorption/emission for the vibration/rotation/translation of one C atom from the chain (Figs. 23.7 and 23.8). Furthermore, there are several signals of smaller intensity (compared to the broad band) which correspond to the fine interactions (resonance) between chains, the condensed structure of polyynes being not a rigid one. The IR spectrum of  $4C_{24}$  polycyclic polyynes shows the stability of the condensed structure, the energy absorbed by atoms being higher than the energy absorbed by the assemblies of atoms.

Searching for new improved materials with various applications among molecules containing carbon atoms has been a subject of research in recent years (Wang et al. 2004, 2014; Trogadas et al. 2014). Cyclic polyynes theoretically studied by have previously predicted heaving optical and electronic properties that could be useful in advanced materials (Ditchfield et al. 1971; Bunz et al. 1999).

## 23.4 Conclusions

In this chapter, we presented a computational chemistry study of cyclic polyynes with an even number of carbon atoms. Our results show that  $C_n$  cyclic polyynes are more likely to be stable when  $n \geq 16$  since starting at this point of energy value, at

STO-3G and 3-21G levels, reaches a plateau. Exponential decay of energy per atom sustains the stability of monocyclic rings at  $C_{24}$ , and a complex of four crossed  $C_{24}$  cycles was identified as a stable and reliable new entity. According to the calculations, it is expected for the identified  $4C_{24}$  complex to have the best hardness among its homologues, being thus a very good candidate for experimental synthesis. Further research will be needed to characterize this new complex.

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