

Is triple crossed C_{28} cyclic polyynes cluster a stable conformation?

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3rd NanoMod

SIM 2023: REINVENTING MANAGEMENT IN TURBULENT TIMES

20-21 October 2023, Timisoara, Romania

Introduction

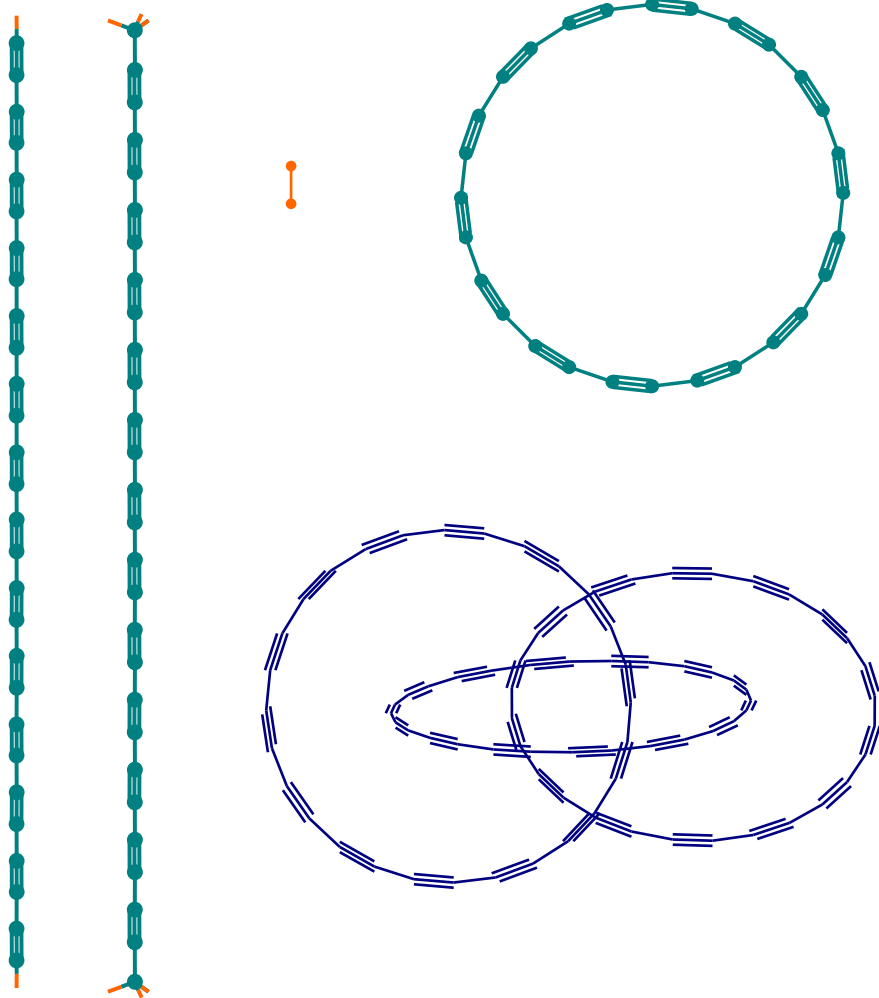
Macromolecule	Formula	Linear	Cyclic	Note
Polyacetylene	$(-\text{HC}=\text{CH}-)_n$	$\text{C}_{28}\text{H}_{30}$	$\text{C}_{28}\text{H}_{28}$	1
Cumulene	$(=\text{C}=\text{C}=\text{C}=\text{C})_n$	C_{26}H_4	C_{26}	2
Polyynes	$(-\text{C}\equiv\text{C}-)_n$	$\text{C}_{28}\text{H}_2, \text{C}_{28}\text{H}_6$	C_{28}	3

¹ High electrical conductivity - Nobel Prize in Chemistry in 2000

² Part of interstellar clouds - DOI 10.1051/0004-6361/202141274

³ C_{44} is the longest known polyynes - DOI 10.1038/nchem.828

Statistical information

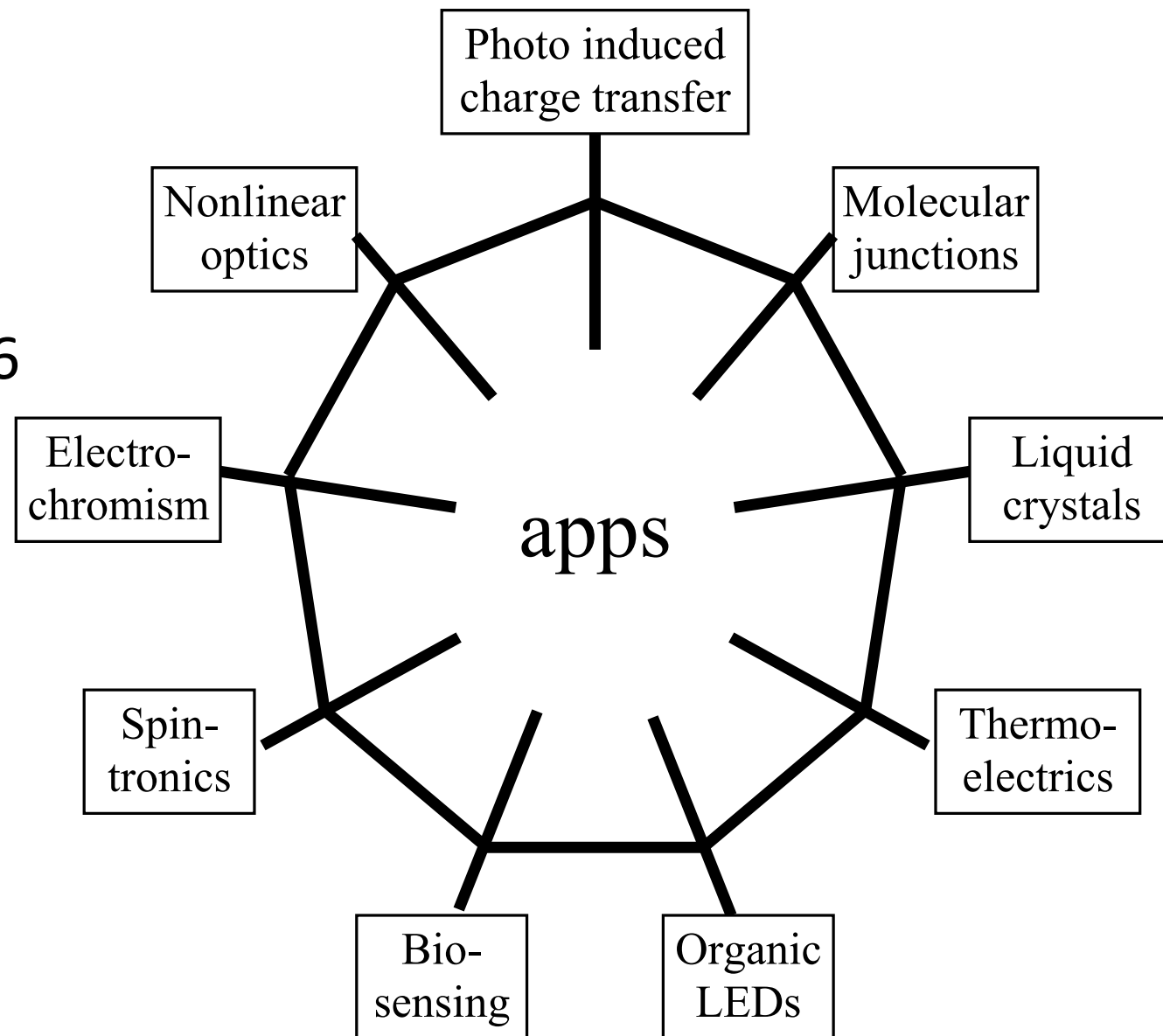


Object	Value	Remark
Total energy (in Hartree):		
H ₂	-1.17505	DFT BP 6-311G* value
C ₂₈ H ₆	-1070.17173	
C ₂₈ H ₂	-1067.68073	
C ₂₈	-1066.45763	
3 C ₂₈ (3×)	-3199.36045	
C–C bond length (in Å):		
C ₂₈ H ₆	1.341	Bonds: 2×1.31, 6×1.32, 2×1.33, 2×1.34, 2×1.45
C ₂₈ H ₂	1.321	Bonds: 5×1.31, 6×1.32, 2×1.33, 2×1.34, 0×1.45
C ₂₈	1.3256	Standard deviation: 4·10 ⁻⁵ Å
3 C ₂₈ (3×)	1.3257	Standard deviation: 1·10 ⁻⁴ Å
C≡C bond length (in Å):		
C ₂₈ H ₆	1.2523	Bonds: 2×1.23, 0×1.24, 4×1.25, 7×1.26
C ₂₈ H ₂	1.2514	Bonds: 2×1.23, 2×1.24, 2×1.25, 8×1.26
C ₂₈	1.2534	Standard deviation: 8·10 ⁻⁶ Å
3 C ₂₈ (3×)	1.2535	Standard deviation: 8·10 ⁻⁵ Å

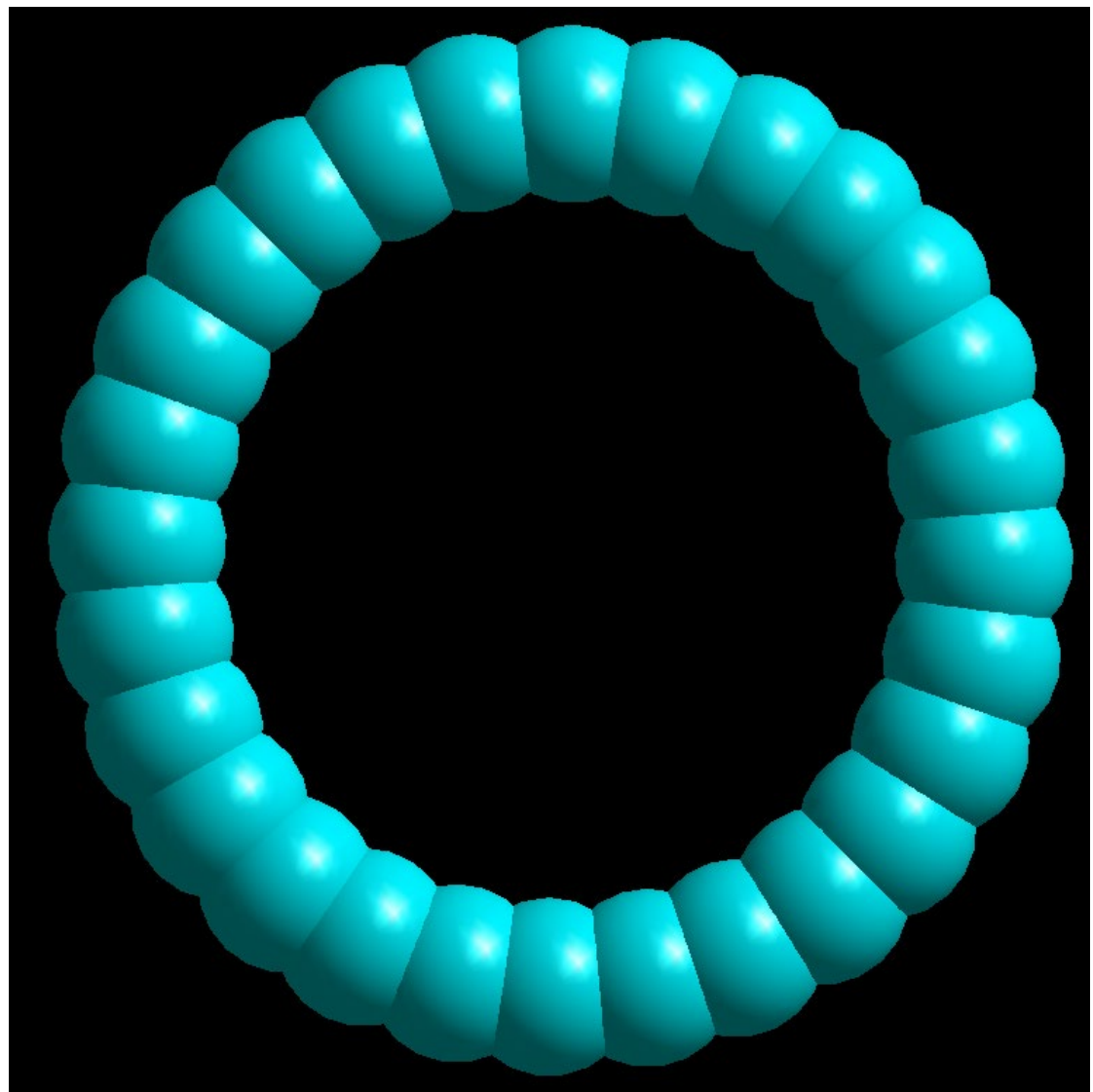
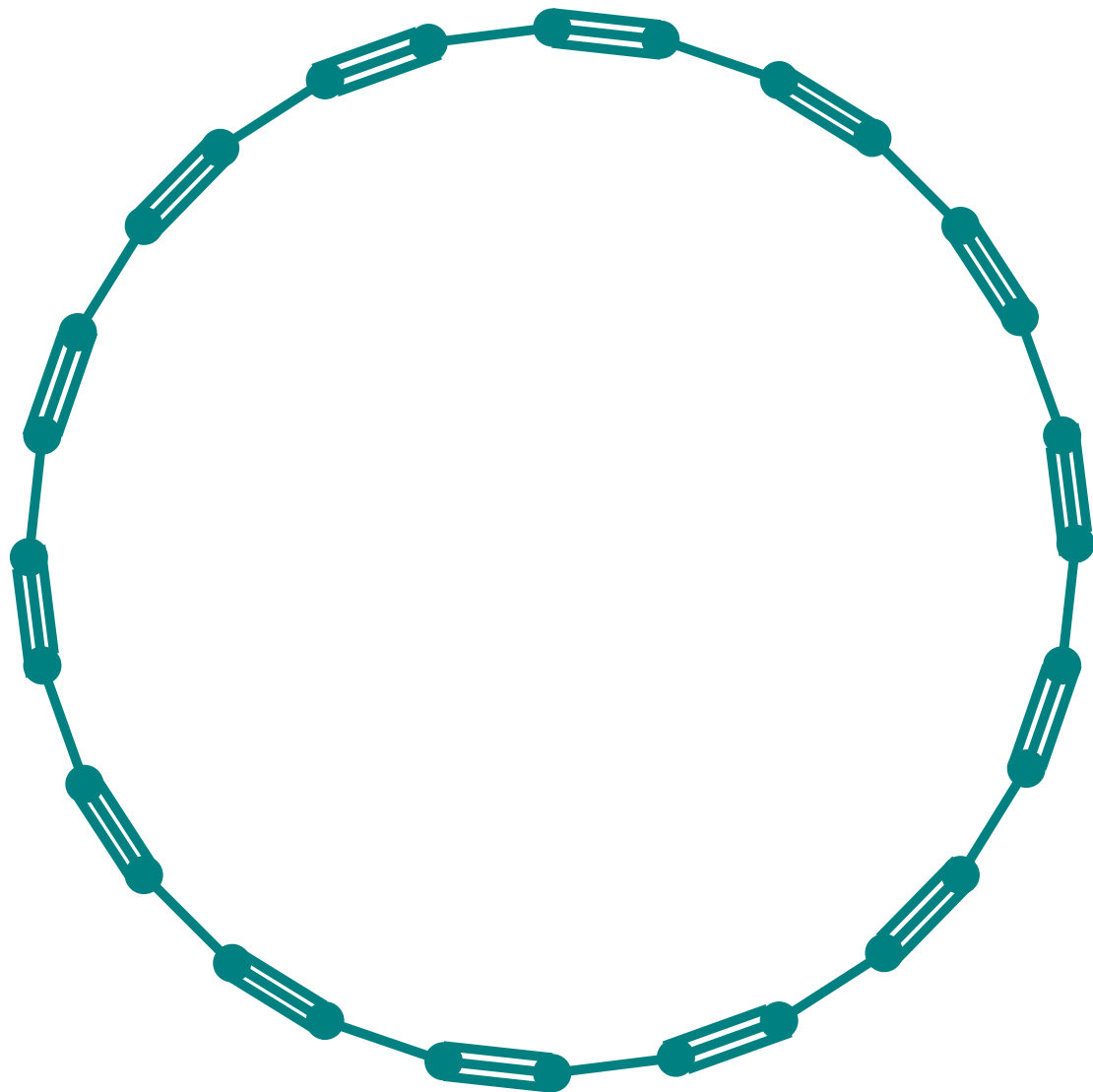
Introduction

• *J. Mater. Chem. C*
2021,9, 10524-10546

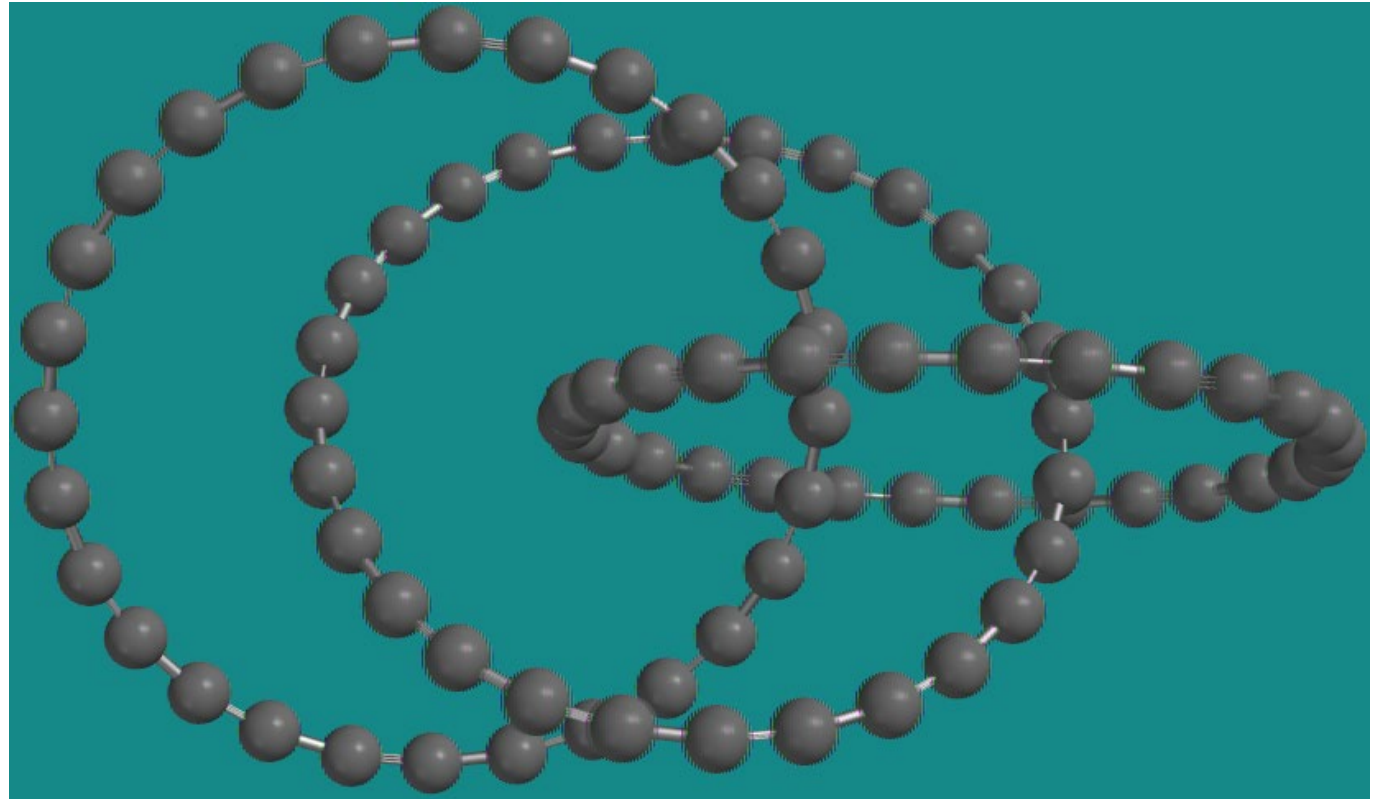
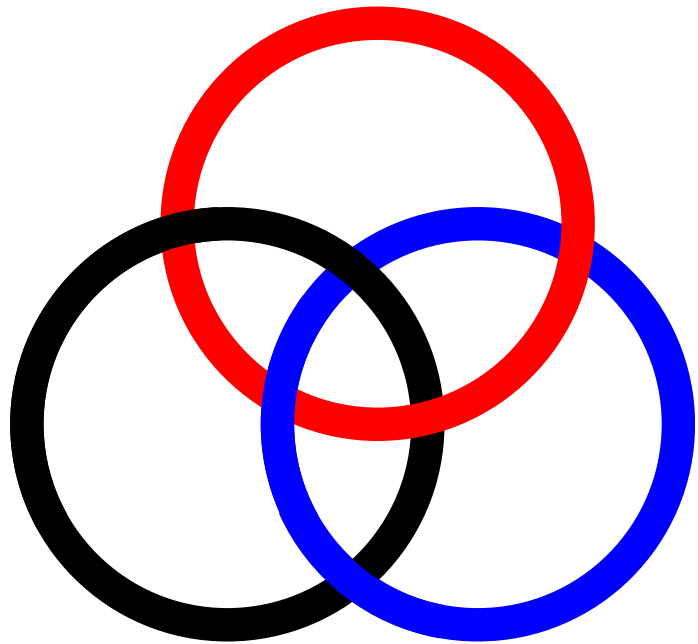
polyynes
or
oligoynes
and
cumulenes



C_{28} cyclic polyiyne



3 C_{28} (3x) cluster



Cluster topology

- Mol 1
 - Atom 1
 - ...
 - Atom 28
- Mol 2
 - Atom 1
 - ...
 - Atom 28
- Mol 3
 - Atom 1
 - ...
 - Atom 28
- Cluster
 - Mol 1 Mol 2 1
 - Mol 1 Mol 3 1
 - Mol 2 Mol 3 1

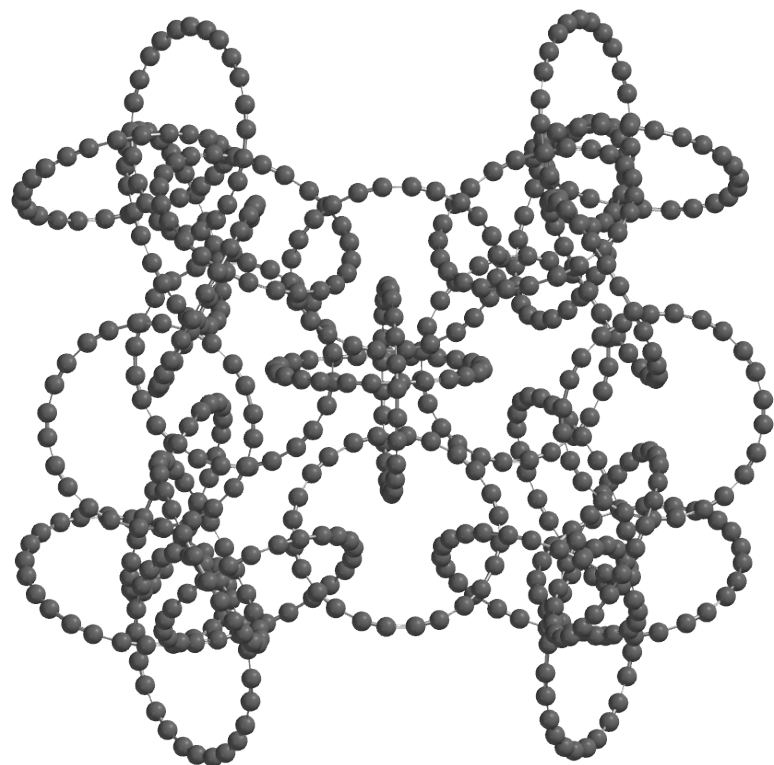
O₃ molecule topology

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Pubmed CID 6206854 SDF file (for O3)
16206854
-OEChem-10182306352D

3 3 0 0 0 0 0 0999 V2000
2.5000 -0.4330 0.0000 O
2.0000 0.4330 0.0000 O
3.0000 0.4330 0.0000 O
1 2 1 0 0 0 0
1 3 1 0 0 0 0
2 3 1 0 0 0 0
M END
```

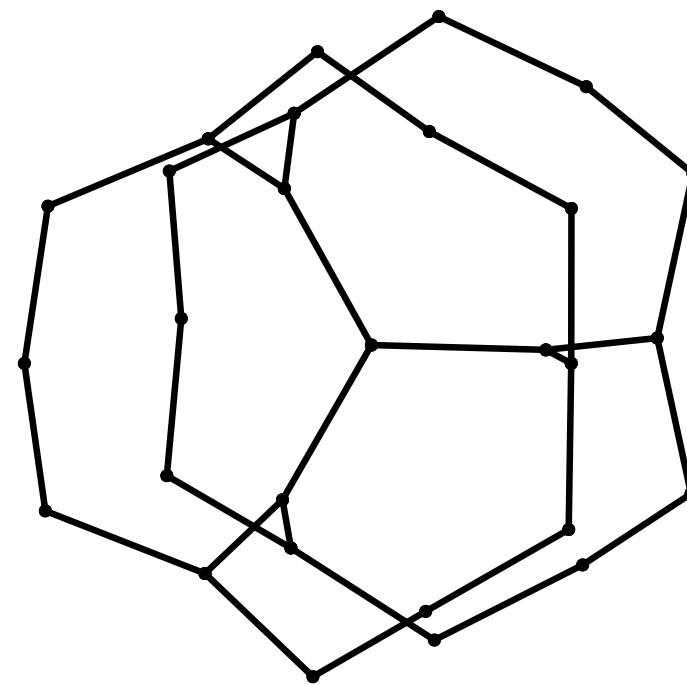
↑ atoms geometry
← molecule topology

A more complex cluster topology



28 C₂₄ cluster

Ref.: DOI 10.1002/qua.25614

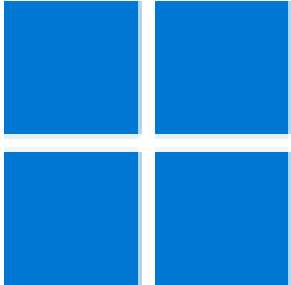

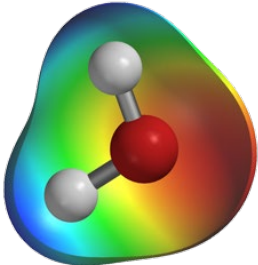





28 C₂₄ topology (all carbon structure
name: tetradehydro-2,12,6:7,1,11-
di(epiheptane[1,4,7]triyl)octalene)

Localization (molecule & cluster geometry)

Schrödinger equation	$\hat{H}\Psi(\vec{r}_1, \dots, \vec{r}_k, t) = i\hbar\frac{\partial}{\partial t}\Psi(\vec{r}_1, \dots, \vec{r}_k, t) + U(t)$
Hartree-Fock (HF) methods	$\Psi_e(\vec{r}_1, \dots, \vec{r}_k) = \text{Imm}_\lambda \begin{pmatrix} \psi_1(\vec{r}_1) & \dots & \psi_{n_e}(\vec{r}_1) \\ \dots & \dots & \dots \\ \psi_1(\vec{r}_{n_e}) & \dots & \psi_{n_e}(\vec{r}_{n_e}) \end{pmatrix}$
Hohenberg and Kohn DFT	$\Psi_e(\vec{r}_1, \dots, \vec{r}_k) = \Psi_{\text{HK}}(\rho(\vec{r}_1, \dots, \vec{r}_k))$
Slater orbitals	$\psi_{e,\text{STO-}n\text{G}}(r; \{\gamma_i, \theta_i\}_{i=1,\dots,4}, \{\delta_k, \epsilon_k\}_{1,\dots,n}) = \sum_{k=1}^n \delta_k r^{\gamma_i} e^{-\epsilon_k r^2} \cos(\theta_i)$

Software

  	HyperChem 8 and Spartan 14 on Windows 10
  	Gaussian 16 on Ubuntu 20 running in a Oracle Virtual Box

- Intensive optimization with Gaussian 16 (84 Carbon atoms):

`%nprocshared=8`

`%mem=32GB`

`%chk=3C28`

`#BP86/6-311G opt=(Tight,Z-matrix)`

Classical vs. symmetry constrained optimization

Optimization	Classical Cartesian	Symmetry constrained
Degrees of freedom	$3 \times (28 \times 3 - 28) = 168$	16 (2 bond lengths + 2 distances + 14 angles)
See (@ gaussian.com):		
÷ molecule specifications (Cartesian, Z-matrix, or a mixture of the two)		
÷ optimization options (Cartesian, Z-matrix, Redundant)		

See supplementary material of Materials Discovery 5: 14 - 21 for a symmetry factor analysis on localization

Z-matrix input files

Topology						
C1						
C2	1	b_1				
C3	2	b_3	1	a_0		
C4	3	b_1	2	a_0	1	d_0
C5	4	b_3	3	a_0	2	d_0
...
C28	27	b_1	26	a_0	25	d_0
C29	28	r_1	27	a_1	26	d_1
C30	29	b_1	28	a_2	27	d_2
C31	30	b_3	29	a_0	28	d_5
C32	31	b_1	30	a_0	29	d_0
...
C56	55	b_1	54	a_0	53	d_0
C57	56	r_2	55	a_3	54	d_3
C58	57	b_1	56	a_4	55	d_4
C59	58	b_3	57	a_0	29	d_6
C84	83	b_1	82	a_0	81	d_0

Topology						
C						
C	1	c_0				
C	2	c_1	1	c_2		
...						
C	$2k+1$	c_0	$2k$	c_2	$2k-1$	c_3
C	$2k+2$	c_1	$2k+1$	c_2	$2k$	c_3
...						
C	1	c_1	2	c_2	3	c_3

Note: $c_0, c_1, c_2,$ and c_3 are numeric floating point values and $k = 1, 2, \dots, 12$.

Note: $a_0, a_1, a_2, a_3, a_4, d_0, d_1, d_2, d_3, d_4, d_5, d_6, r_1, r_2, b_1,$ and b_3 are numeric (floating point) values.

Table 2. DFT BP 6-311G* minimized energy data.

Object	Value
Total energy (in Hartree):	
H ₂	-1.17505
C ₂₈ H ₆	-1070.17173
C ₂₈ H ₂	-1067.68073
C ₂₈	-1066.45763
3C ₂₈ (3×)	-3199.36045
C – C bond length (in Å):	
C ₂₈ H ₆	1.341
C ₂₈ H ₂	1.321
C ₂₈	1.3256
3C ₂₈ (3×)	1.3257
C ≡ C bond length (in Å):	
C ₂₈ H ₆	1.2523
C ₂₈ H ₂	1.2514
C ₂₈	1.2534
3 C ₂₈ (3×)	1.2535
Highest occupied molecular orbital energy (HOMO, in eV):	
C ₂₈ H ₆	-5.40
C ₂₈ H ₂	-5.65
C ₂₈	-5.55
3 C ₂₈ (3×)	-5.52

Ab initio HF results for $3C_{28}(3x)$ cluster

Variable	Initial values			Optimized values			
	Basis set	STO-3G	STO-6G	3-21G	STO-3G	STO-6G	3-21G
a_1 (°)		62.3	66.79	67.5572	66.79	67.5572	68.8227
a_2 (°)		32.6	31.525	30.7715	31.525	30.7715	31.103
a_3 (°)		93.9	99.8835	100.7864	99.8835	100.7864	101.8435
a_4 (°)		73.4	67.8085	66.3221	67.8085	66.3221	73.1824
d_1 (°)		9.2	20.8758	21.8711	20.8758	21.8711	18.7214
d_2 (°)		264.5	288.0992	293.8228	288.0992	293.8228	304.1934
d_3 (°)		336	352.3978	352.396	352.3978	352.396	350.0585
d_4 (°)		101.7	79.8583	80.3866	79.8583	80.3866	86.638
d_5 (°)		252.1	259.5932	264.1909	259.5932	264.1909	282.1058
d_6 (°)		9.2	41.8704	44.3725	41.8704	44.3725	45.0033
r_1 (Å)		5.9	6.6069	6.8445	6.6069	6.8445	7.3985
r_2 (Å)		4.9	4.5177	4.6059	4.5177	4.6059	4.5938
b_1 (Å)		1.3586	1.3974	1.397	1.3974	1.397	1.3616
b_3 (Å)		1.2188	1.1866	1.1849	1.1866	1.1849	1.1969

Note: In each subsequent basis set, the initial values for the *ab-initio* optimization are taken from the optimized values of the previous basis set.

DFT BP results for $3C_{28}(3x)$ cluster

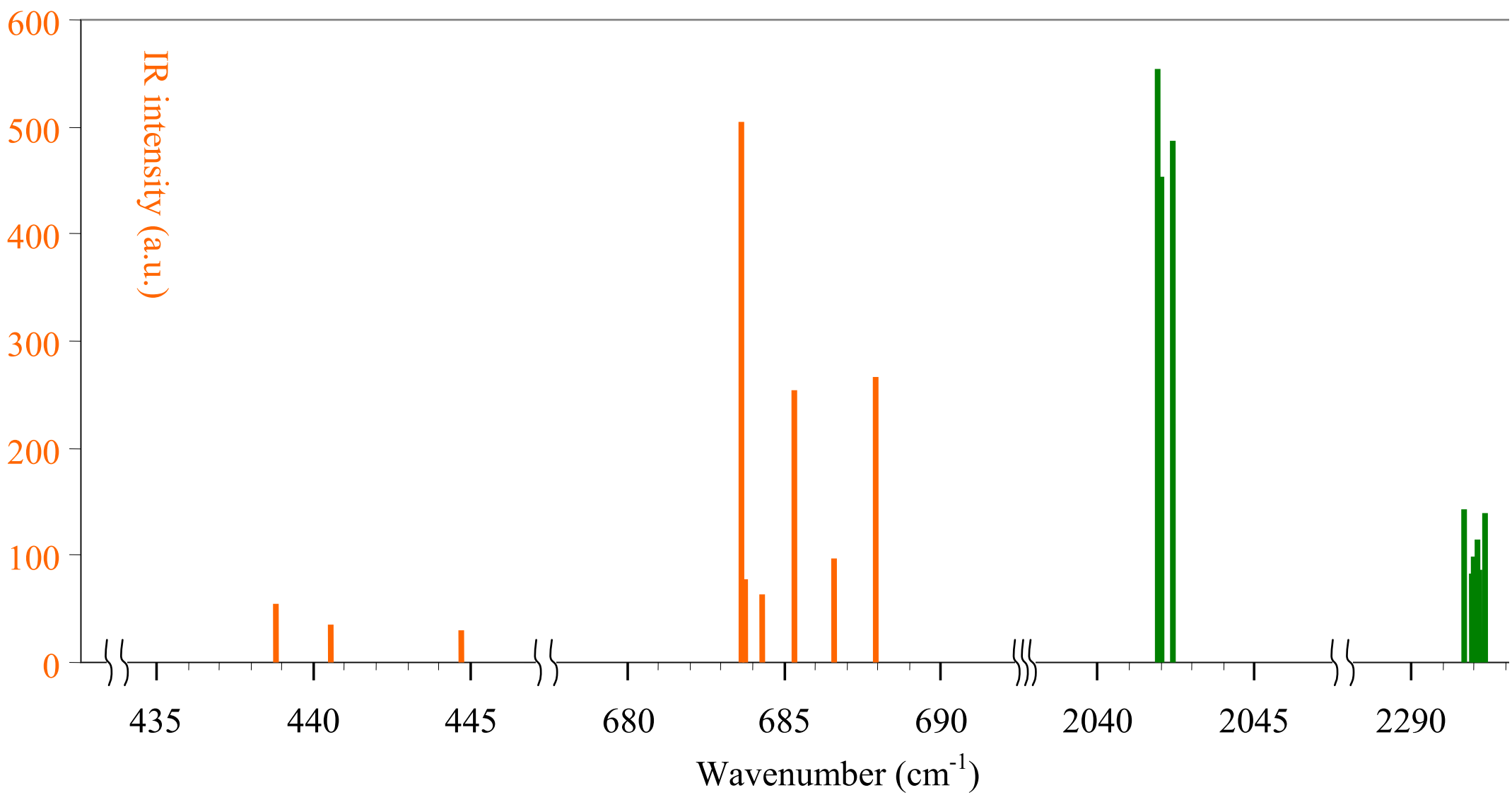
Variable	Initial values			Optimized values			
	Basis set	STO-3G	STO-6G	3-21G	STO-3G	STO-6G	3-21G
a_1 (°)		62.3	65.1494	65.0223	65.1494	65.0223	65.7197
a_2 (°)		32.6	43.8036	44.0403	43.8036	44.0403	45.0451
a_3 (°)		93.9	99.3011	98.9842	99.3011	98.9842	98.1413
a_4 (°)		73.4	66.8137	66.5817	66.8137	66.5817	65.6638
d_1 (°)		9.2	12.9403	13.0418	12.9403	13.0418	13.9321
d_2 (°)		264.5	273.2732	273.1815	273.2732	273.1815	274.306
d_3 (°)		336	350.7954	350.9283	350.7954	350.9283	356.6947
d_4 (°)		101.7	72.9921	72.3379	72.9921	72.3379	71.3572
d_5 (°)		252.1	254.6475	254.4274	254.6475	254.4274	252.8502
d_6 (°)		9.2	21.0582	20.4029	21.0582	20.4029	20.8467
r_1 (Å)		5.9	5.9349	5.9037	5.9349	5.9037	5.8302
r_2 (Å)		4.9	4.3368	4.3552	4.3368	4.3552	4.1621
b_1 (Å)		1.3586	1.3535	1.3533	1.3535	1.3533	1.326
b_3 (Å)		1.2188	1.2637	1.2637	1.2637	1.2637	1.2555

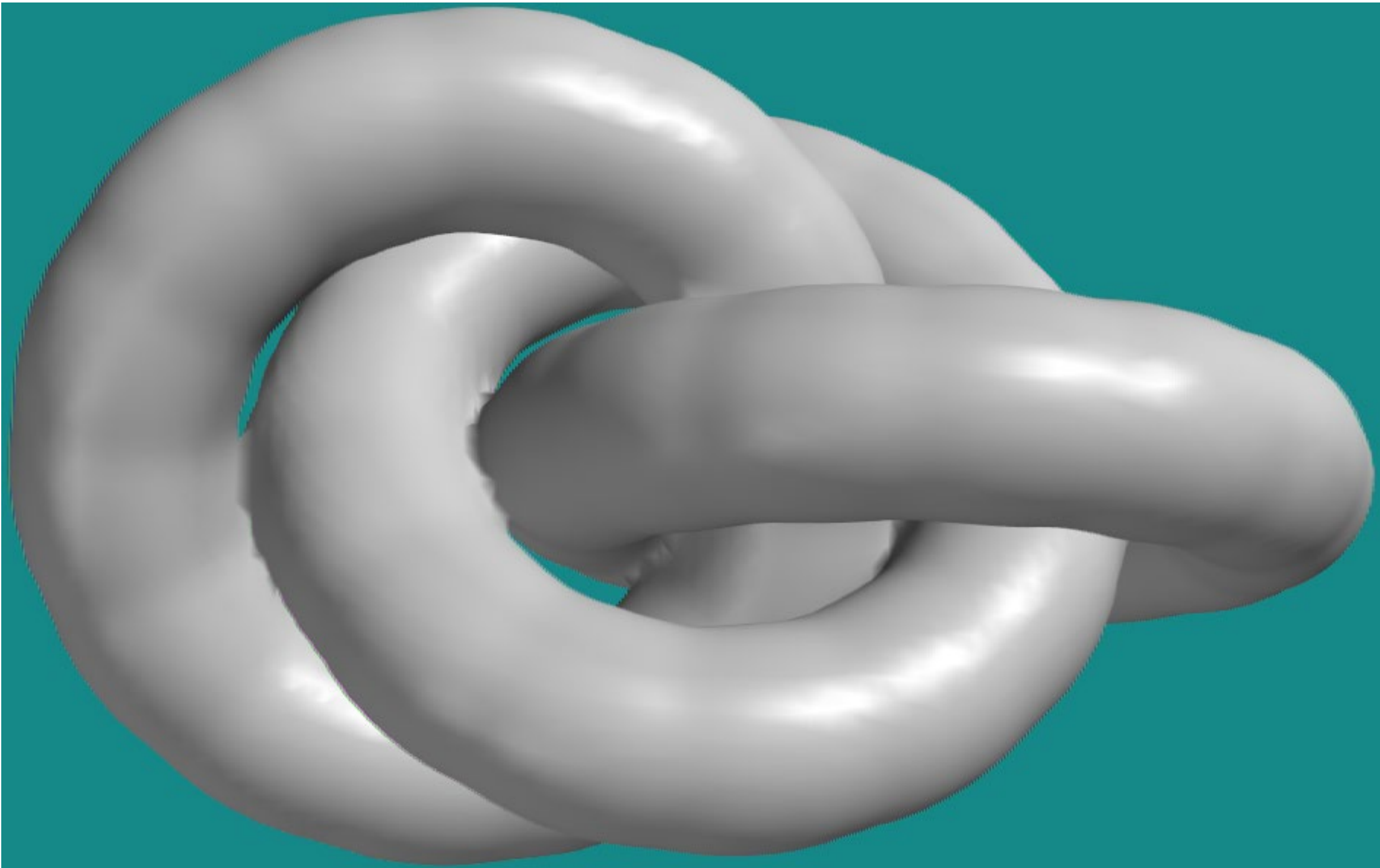
Note: In each subsequent basis set, the initial values for the DFT optimization are taken from the optimized values of the previous basis set.

Table 3. Cluster conformation from DFT BP 6-311G* minimized energy data.

Parameter	Value
Center coordinates ((x,y,z), in Å, ± standard deviation):	
mol 1	(+3.846 \pm 0.006, - 0.115 \pm 0.006, - 0.040 \pm 0.006)
mol 2	(-0.024 \pm 0.035, + 0.220 \pm 0.035, + 0.069 \pm 0.035)
mol 3	(-3.824 \pm 0.035, - 0.121 \pm 0.006, - 0.025 \pm 0.035)
Molecular torus radius (in Å, ± standard deviation):	
mol 1	5.759 \pm 0.011
mol 2	5.758 \pm 0.061
mol 3	5.759 \pm 0.011
Versors ((v _x , v _y , v _z), in Å, ± standard deviation):	
mol 1	(-0.029 \pm 0.024, - 0.873 \pm 0.011, - 0.487 \pm 0.018)
mol 2	(+0.039 \pm 0.023, - 0.999 \pm 0.022, + 0.023 \pm 0.001)
mol 3	(+0.031 \pm 0.020, - 0.874 \pm 0.009, + 0.484 \pm 0.016)
Rotation angle on Oz, in °, to get first atom on Ox:	
mol 1	2.40
mol 2	-13.48
mol 3	1.76
In between angles, in °, ± standard deviation):	
mol 1 vs. mol 2	60.5 \pm 0.06
mol 1 vs. mol 3	58.2 \pm 0.05
mol 2 vs. mol 3	61.7 \pm 0.05

Note: All atoms have the coordinates given in Appendix 4: mol 1 is defined by the first 28 lines; mol 2 is defined by lines 29–56; mol 3 is defined by lines 57–84.

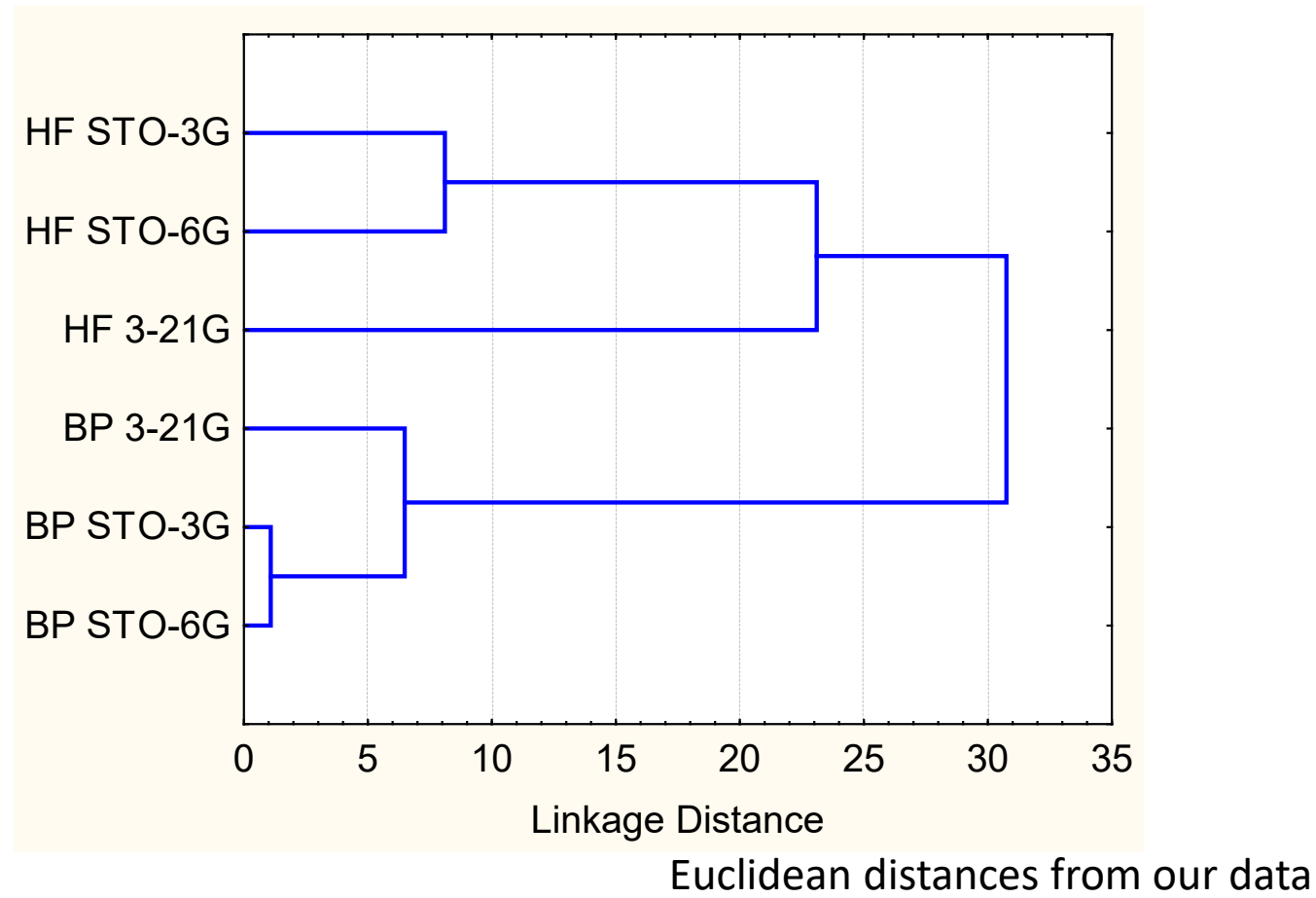




Cluster statistics

Parameter	Value
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Association between optimization methods



Conclusions

- Bending of polyynes is a difficult task, and crossing rings of polyynes is even more challenging
- the total energy of 3 $C_{28}(3\times)$ differs from the total energy of system of 3 isolated C_{28} by about 0.01 Hartree \Rightarrow 3 $C_{28}(3\times)$ stable configuration
- The angles between the planes of the molecular rings (60.5 °, 58.2 °, and 61.7 °) reveal almost an axial alignment of the rings very close to a C_3 symmetry

Thanks

- For the opportunity to present the results
- For your attention (patience)

