

–Supplementary Material–
**Stability of the Polyynic Form of C₁₈, C₂₂,
C₂₆, and C₃₀ Nanorings: A Challenge
Tackled by Range-Separated
Double-Hybrid Density Functionals**

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Running a RSX-QIDH calculation

A RSX-QIDH single-point calculation can be run with the following route card, omitting basis set specification and any other option, using the GAUSSIAN'16 (C.01 release) program:

```
#P PBEQIDH IOP(3/74=1001009,3/78=0666606666,3/107=0270000000,  
3/108=0270000000,3/119=0310000000,3/120=0310000000,  
3/125=0333403334,3/130=06900,3/131=06900)
```

Details of the Monte Carlo calculations

Table S1: Total number of variationally optimized parameters (M) of the VMC calculations for each molecule.

Molecule	M
C ₁₈ polyynic	1204
C ₁₈ cumulenic	1062
C ₂₂ polyynic	1218
C ₂₂ cumulenic	1190
C ₂₆ polyynic	1378
C ₂₆ cumulenic	646

Table S2: Values of $\Delta E(C_n)$ (kcal/mol) for the systems studied, with the BFD pseudopotential and the VTZ basis sets.

Method	C ₁₈	C ₂₂	C ₂₆	MSD	MAD	RMSD
CASSCF	-0.758	-1.722	-2.532	-1.09	1.09	1.19
CASSCF-SOCI	-0.692	-1.505	-2.265	-0.91	0.91	0.99
Reference	-0.27 ± 0.02	-0.58 ± 0.02	-0.89 ± 0.02			

Table S3: Absolute energy values (in E_h) and their uncertainties for the systems studied, at the DMC level.

Molecule	$E(C_n; \text{cumulenic})$	$E(C_n; \text{polyynic})$
C ₁₈	-101.674968 ± 0.000325	-101.682724 ± 0.000332
C ₂₂	-124.291386 ± 0.000380	-124.311847 ± 0.000397
C ₂₆	-146.902668 ± 0.000458	-146.939596 ± 0.000506

All results for C_{30}

Table S4: Values of $\Delta E(C_n)$ (kcal/mol) for C_{30} , with the def2-QZVP basis sets.

	Method	C_{30}
	PBE	0.941
GH functionals	B3LYP	0.093
	PBE0	-0.044
	PBE0-1/3	-0.444
	M06-2X	-1.388
DH functionals	PBE0-DH	-0.112
	B2-PLYP	1.054
	B2GP-PLYP	1.087
	PBE-QIDH	0.598
SOS-DH functionals	DSD-PBEP86	0.688
	SOS1-QIDH	-0.799

Atomic cartesian coordinates

Table S5: Cartesian coordinates of C₁₈ cumulenic form.

C	0.000000	3.662004	0.000000
C	1.252479	3.441158	0.000000
C	2.353891	2.805258	0.000000
C	3.171388	1.831002	0.000000
C	3.606370	0.635900	0.000000
C	3.606370	-0.635900	0.000000
C	3.171388	-1.831002	0.000000
C	2.353891	-2.805258	0.000000
C	1.252479	-3.441158	0.000000
C	-0.000000	-3.662004	0.000000
C	-1.252479	-3.441158	0.000000
C	-2.353891	-2.805258	0.000000
C	-3.171388	-1.831002	0.000000
C	-3.606370	-0.635900	0.000000
C	-3.606370	0.635900	0.000000
C	-3.171388	1.831002	0.000000
C	-2.353891	2.805258	0.000000
C	-1.252479	3.441158	0.000000

Table S6: Cartesian coordinates of C₁₈ polyynic form.

C	0.000000	0.609809	-3.635424
C	0.000000	1.869910	-3.176949
C	0.000000	2.804183	-2.393056
C	0.000000	3.474620	-1.231846
C	0.000000	3.686373	-0.030779
C	0.000000	3.453489	1.289685
C	0.000000	2.843647	2.345862
C	0.000000	1.816475	3.207701
C	0.000000	0.670419	3.624806
C	0.000000	-0.670419	3.624806
C	0.000000	-1.816475	3.207701
C	0.000000	-2.843647	2.345862
C	0.000000	-3.453489	1.289685
C	0.000000	-3.686373	-0.030779
C	0.000000	-3.474620	-1.231846
C	0.000000	-2.804183	-2.393056
C	0.000000	-1.869910	-3.176949
C	0.000000	-0.609809	-3.635424

Table S7: Cartesian coordinates of C₂₂ cumulenic form.

C	0.000000	4.466246	0.000000
C	1.258287	4.285332	0.000000
C	2.414635	3.757245	0.000000
C	3.375363	2.924769	0.000000
C	4.062640	1.855346	0.000000
C	4.420786	0.635613	0.000000
C	4.420786	-0.635613	0.000000
C	4.062640	-1.855346	0.000000
C	3.375363	-2.924769	0.000000
C	2.414635	-3.757245	0.000000
C	1.258287	-4.285332	0.000000
C	-0.000000	-4.466246	0.000000
C	-1.258287	-4.285332	0.000000
C	-2.414635	-3.757245	0.000000
C	-3.375363	-2.924769	0.000000
C	-4.062640	-1.855346	0.000000
C	-4.420786	-0.635613	0.000000
C	-4.420786	0.635613	0.000000
C	-4.062640	1.855346	0.000000
C	-3.375363	2.924769	0.000000
C	-2.414635	3.757245	0.000000
C	-1.258287	4.285332	0.000000

Table S8: Cartesian coordinates of C_{22} polyynic form.

C	0.000000	-0.607675	-4.458668
C	0.000000	-1.899366	-4.079433
C	0.000000	-2.921776	-3.422378
C	0.000000	-3.803384	-2.404975
C	0.000000	-4.308252	-1.299471
C	0.000000	-4.499838	0.033059
C	0.000000	-4.326872	1.236019
C	0.000000	-3.767621	2.460591
C	0.000000	-2.971741	3.379072
C	0.000000	-1.839218	4.106894
C	0.000000	-0.673114	4.449289
C	0.000000	0.673114	4.449289
C	0.000000	1.839218	4.106894
C	0.000000	2.971741	3.379072
C	0.000000	3.767621	2.460591
C	0.000000	4.326872	1.236019
C	0.000000	4.499838	0.033059
C	0.000000	4.308252	-1.299471
C	0.000000	3.803384	-2.404975
C	0.000000	2.921776	-3.422378
C	0.000000	1.899366	-4.079433
C	0.000000	0.607675	-4.458668

Table S9: Cartesian coordinates of C₂₆ cumulenenic form.

C	0.000000	5.272423	0.000000
C	1.261773	5.119216	0.000000
C	2.450217	4.668499	0.000000
C	3.496263	3.946465	0.000000
C	4.339119	2.995078	0.000000
C	4.929801	1.869627	0.000000
C	5.233981	0.635520	0.000000
C	5.233981	-0.635520	0.000000
C	4.929801	-1.869627	0.000000
C	4.339119	-2.995078	0.000000
C	3.496263	-3.946465	0.000000
C	2.450217	-4.668499	0.000000
C	1.261773	-5.119216	0.000000
C	-0.000000	-5.272423	0.000000
C	-1.261773	-5.119216	0.000000
C	-2.450217	-4.668499	0.000000
C	-3.496263	-3.946465	0.000000
C	-4.339119	-2.995078	0.000000
C	-4.929801	-1.869627	0.000000
C	-5.233981	-0.635520	0.000000
C	-5.233981	0.635520	0.000000
C	-4.929801	1.869627	0.000000
C	-4.339119	2.995078	0.000000
C	-3.496263	3.946465	0.000000
C	-2.450217	4.668499	0.000000
C	-1.261773	5.119216	0.000000

Table S10: Cartesian coordinates of C₂₆ polyynic form.

C	0.000000	0.606904	-5.277758
C	0.000000	1.915367	-4.955277
C	0.000000	2.990176	-4.391202
C	0.000000	3.998950	-3.497635
C	0.000000	4.688553	-2.498718
C	0.000000	5.166452	-1.238677
C	0.000000	5.312777	-0.033697
C	0.000000	5.150323	1.304099
C	0.000000	4.719863	2.439041
C	0.000000	3.954281	3.548082
C	0.000000	3.045681	4.352964
C	0.000000	1.852389	4.979176
C	0.000000	0.673811	5.269602
C	0.000000	-0.673811	5.269602
C	0.000000	-1.852389	4.979176
C	0.000000	-3.045681	4.352964
C	0.000000	-3.954281	3.548082
C	0.000000	-4.719863	2.439041
C	0.000000	-5.150323	1.304099
C	0.000000	-5.312777	-0.033697
C	0.000000	-5.166452	-1.238677
C	0.000000	-4.688553	-2.498718
C	0.000000	-3.998950	-3.497635
C	0.000000	-2.990176	-4.391202
C	0.000000	-1.915367	-4.955277
C	0.000000	-0.606904	-5.277758

Table S11: Cartesian coordinates of C₃₀ cumulenenic form.

C	-0.000000	6.078424	0.000000
C	1.263775	5.945595	0.000000
C	2.472318	5.552916	0.000000
C	3.572808	4.917548	0.000000
C	4.517149	4.067259	0.000000
C	5.264069	3.039212	0.000000
C	5.780924	1.878336	0.000000
C	6.045125	0.635368	0.000000
C	6.045125	-0.635368	0.000000
C	5.780924	-1.878336	0.000000
C	5.264069	-3.039212	0.000000
C	4.517149	-4.067259	0.000000
C	3.572808	-4.917548	0.000000
C	2.472318	-5.552916	0.000000
C	1.263775	-5.945595	0.000000
C	-0.000000	-6.078424	0.000000
C	-1.263775	-5.945595	0.000000
C	-2.472318	-5.552916	0.000000
C	-3.572808	-4.917548	0.000000
C	-4.517149	-4.067259	0.000000
C	-5.264069	-3.039212	0.000000
C	-5.780924	-1.878336	0.000000
C	-6.045125	-0.635368	0.000000
C	-6.045125	0.635368	0.000000
C	-5.780924	1.878336	0.000000
C	-5.264069	3.039212	0.000000
C	-4.517149	4.067259	0.000000
C	-3.572808	4.917548	0.000000
C	-2.472318	5.552916	0.000000
C	-1.263775	5.945595	0.000000

Table S12: Cartesian coordinates of C₃₀ polyynic form.

C	-5.287746	3.092058	0.000000
C	-5.835903	1.860605	0.000000
C	-6.088064	0.673944	0.000000
C	-6.088143	-0.673998	0.000000
C	-5.835989	-1.860661	0.000000
C	-5.287760	-3.092080	0.000000
C	-4.574703	-4.073559	0.000000
C	-3.572996	-4.975519	0.000000
C	-2.522374	-5.582104	0.000000
C	-1.240402	-5.998632	0.000000
C	-0.033890	-6.125431	0.000000
C	1.306666	-5.984513	0.000000
C	2.460440	-5.609607	0.000000
C	3.627784	-4.935619	0.000000
C	4.529325	-4.123848	0.000000
C	5.321616	-3.033332	0.000000
C	5.815042	-1.925054	0.000000
C	6.095288	-0.606565	0.000000
C	6.095287	0.606592	0.000000
C	5.815042	1.925081	0.000000
C	5.321615	3.033357	0.000000
C	4.529326	4.123875	0.000000
C	3.627785	4.935646	0.000000
C	2.460440	5.609631	0.000000
C	1.306665	5.984536	0.000000
C	-0.033890	6.125466	0.000000
C	-1.240401	5.998649	0.000000
C	-2.522347	5.582041	0.000000
C	-3.572977	4.975470	0.000000
C	-4.574738	4.073570	0.000000