Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting information for: Energetic and Spectroscopic Properties of the Low-lying C_7H_2 Isomers: A High-Level Ab Initio Perspective

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Table S1: Optimized geometries of the triplet ground electronic state ($\widetilde{X}^3\Sigma_g^-$) of heptatriynylidene (**1**) in Cartesian coordinates (in Ångström units) obtained using ROHF wavefunction at different levels within $D_{\infty h}$ point group symmetry.

ROMP2/cc-pVDZ				ROMP2/cc-pVTZ			
C	0.000000	0.000000	0.000000	C	0.000000	0.000000	0.000000
C	0.000000	0.000000	-1.297870	C	0.000000	0.000000	-1.282305
C	0.000000	0.000000	1.297870	C	0.000000	0.000000	1.282305
C	0.000000	0.000000	-2.635356	C	0.000000	0.000000	-2.603030
C	0.000000	0.000000	2.635356	C	0.000000	0.000000	2.603030
C	0.000000	0.000000	-3.892105	C	0.000000	0.000000	-3.843015
C	0.000000	0.000000	3.892105	C	0.000000	0.000000	3.843015
H	0.000000	0.000000	-4.968860	H	0.000000	0.000000	-4.905689
H	0.000000	0.000000	4.968860	H	0.000000	0.000000	4.905689
ROCCSD/cc-pVDZ				ROCCSD/cc-pVTZ			
C	0.000000	0.000000	0.000000	C	0.000000	0.000000	0.000000
C	0.000000	0.000000	-1.289228	C	0.000000	0.000000	-1.271573
C	0.000000	0.000000	1.289228	C	0.000000	0.000000	1.271573
C	0.000000	0.000000	-2.646621	C	0.000000	0.000000	-2.612506
C	0.000000	0.000000	2.646621	C	0.000000	0.000000	2.612506
C	0.000000	0.000000	-3.887124	C	0.000000	0.000000	-3.833933
C	0.000000	0.000000	3.887124	C	0.000000	0.000000	3.833933
H	0.000000	0.000000	-4.965033	H	0.000000	0.000000	-4.896144
H	0.000000	0.000000	4.965033	H	0.000000	0.000000	4.896144
ROCCSD(T)/cc-pVDZ				ROCCSD(T)/cc-pVTZ			
C	0.000000	0.000000	0.000000	C	0.000000	0.000000	0.000000
C	0.000000	0.000000	-1.295470	C	0.000000	0.000000	-1.278245
C	0.000000	0.000000	1.295470	C	0.000000	0.000000	1.278245
C	0.000000	0.000000	-2.648320	C	0.000000	0.000000	-2.614468
C	0.000000	0.000000	2.648320	C	0.000000	0.000000	2.614468
C	0.000000	0.000000	-3.898848	C	0.000000	0.000000	-3.846509
C	0.000000	0.000000	3.898848	C	0.000000	0.000000	3.846509
H	0.000000	0.000000	-4.978463	H	0.000000	0.000000	-4.910727
H	0.000000	0.000000	4.978463	H	0.000000	0.000000	4.910727

Table S2: Optimized geometries of the triplet ground electronic state ($\widetilde{X}^3\Sigma_g^-$) of heptatriynylidene (**1**) in Cartesian coordinates (in Ångström units) obtained using UHF wavefunction at different levels within $D_{\infty h}$ point group symmetry.

UMP2/cc-pVDZ				UMP2/cc-pVTZ			
C	0.000000	0.000000	0.000000	C	0.000000	0.000000	0.000000
C	0.000000	0.000000	-1.272192	C	0.000000	0.000000	-1.254876
C	0.000000	0.000000	1.272192	C	-0.000000	0.000000	1.254876
C	0.000000	0.000000	-2.631536	C	0.000000	-0.000000	-2.602037
C	0.000000	0.000000	2.631536	C	-0.000000	-0.000000	2.602037
C	0.000000	0.000000	-3.841107	C	0.000000	-0.000000	-3.793320
C	0.000000	0.000000	3.841107	C	-0.000000	-0.000000	3.793320
H	0.000000	0.000000	-4.915721	H	0.000000	-0.000000	-4.853584
H	0.000000	0.000000	4.915721	H	-0.000000	-0.000000	4.853584
UCCSD/cc-pVDZ				UCCSD/cc-pVTZ			
C	0.000000	0.000000	0.000000	C	0.000000	0.000000	0.000000
C	0.000000	0.000000	-1.289915	C	0.000000	0.000000	-1.272305
C	0.000000	0.000000	1.289915	C	-0.000000	0.000000	1.272305
C	0.000000	0.000000	-2.645837	C	0.000000	-0.000000	-2.611820
C	0.000000	0.000000	2.645837	C	-0.000000	-0.000000	2.611820
C	0.000000	0.000000	-3.887329	C	0.000000	-0.000000	-3.834155
C	0.000000	0.000000	3.887329	C	-0.000000	-0.000000	3.834155
H	0.000000	0.000000	-4.965060	H	0.000000	-0.000000	-4.896238
H	0.000000	0.000000	4.965060	H	-0.000000	-0.000000	4.896238
UCCSD(T)/cc-pVDZ				UCCSD(T)/cc-pVTZ			
C	0.000000	0.000000	0.000000	C	0.000000	0.000000	0.000000
C	0.000000	0.000000	-1.292404	C	0.000000	0.000000	-1.275220
C	0.000000	0.000000	1.292404	C	-0.000000	0.000000	1.275220
C	0.000000	0.000000	-2.647811	C	0.000000	-0.000000	-2.614216
C	0.000000	0.000000	2.647811	C	-0.000000	-0.000000	2.614216
C	0.000000	0.000000	-3.893694	C	0.000000	-0.000000	-3.841688
C	0.000000	0.000000	3.893694	C	-0.000000	-0.000000	3.841688
H	0.000000	0.000000	-4.972870	H	0.000000	-0.000000	-4.905545
H	0.000000	0.000000	4.972870	H	-0.000000	-0.000000	4.905545

Table S3: Optimized geometries of the singlet ground electronic state ($\widetilde{X}^1A'$) of 1-(buta-1,3-diynyl)cyclopropenylidene (**2**) in Cartesian coordinates (in Ångström units) obtained at different levels within C_s point group symmetry.

MP2/cc-pVDZ				MP2/cc-pVTZ			
C	-1.574729	-0.011289	0.000000	C	-1.556466	-0.005955	0.000000
C	-0.174058	0.008588	0.000000	C	-0.170085	0.008487	0.000000
C	1.068955	-0.001595	0.000000	C	1.056444	0.002099	0.000000
C	2.445681	0.001678	0.000000	C	2.417867	0.003159	0.000000
C	3.684166	0.001855	0.000000	C	3.638712	0.000038	0.000000
H	4.760906	0.002336	0.000000	H	4.701063	-0.001800	0.000000
C	-2.758018	0.650684	0.000000	C	-2.732829	0.636913	0.000000
C	-2.816304	-0.785258	0.000000	C	-2.774274	-0.776720	0.000000
H	-3.280813	1.609108	0.000000	H	-3.264743	1.573245	0.000000
CCSD/cc-pVDZ				CCSD/cc-pVTZ			
C	-1.581346	-0.011929	0.000000	C	-1.562236	-0.007438	0.000000
C	-0.168120	0.004599	0.000000	C	-0.163467	0.004455	0.000000
C	1.060926	-0.002287	0.000000	C	1.047239	0.001332	0.000000
C	2.453648	0.001613	0.000000	C	2.424151	0.002914	0.000000
C	3.680030	0.002965	0.000000	C	3.631403	0.001437	0.000000
H	4.758124	0.004072	0.000000	H	4.693620	0.000279	0.000000
C	-2.752598	0.652322	0.000000	C	-2.724804	0.638571	0.000000
C	-2.817542	-0.783155	0.000000	C	-2.773424	-0.773723	0.000000
H	-3.269762	1.613734	0.000000	H	-3.251253	1.576810	0.000000
CCSD(T)/cc-pVDZ				CCSD(T)/cc-pVTZ			
C	-1.581224	-0.012093	0.000000	C	-1.562093	-0.007103	0.000000
C	-0.170833	0.007363	0.000000	C	-0.166483	0.006825	0.000000
C	1.067702	-0.003011	0.000000	C	1.054324	0.001199	0.000000
C	2.456158	0.001457	0.000000	C	2.426848	0.002799	0.000000
C	3.690816	0.002027	0.000000	C	3.642879	0.000367	0.000000
H	4.770512	0.003317	0.000000	H	4.706974	-0.000995	0.000000
C	-2.760055	0.654605	0.000000	C	-2.733126	0.640789	0.000000
C	-2.828357	-0.786772	0.000000	C	-2.784169	-0.777792	0.000000
H	-3.272722	1.621056	0.000000	H	-3.256480	1.583600	0.000000

Table S4: Optimized geometries of the singlet ground electronic state ($\widetilde{X}^1A_1$) of 1,2-(diethynyl)cyclopropenylidene (**3**) in Cartesian coordinates (in Ångström units) obtained at different levels within C_{2v} point group symmetry.

MP2/cc-pVDZ				MP2/cc-pVTZ			
C	0.000000	1.880568	0.279351	C	0.000000	1.868047	0.272863
C	0.000000	0.681713	-0.456734	C	0.000000	0.673925	-0.442265
C	0.000000	0.000000	-1.739280	C	0.000000	0.000000	-1.703492
C	0.000000	-0.681713	-0.456734	C	0.000000	-0.673925	-0.442265
C	0.000000	-1.880568	0.279351	C	0.000000	-1.868047	0.272863
C	0.000000	-2.935181	0.922724	C	0.000000	-2.911725	0.900258
C	0.000000	2.935181	0.922724	C	0.000000	2.911725	0.900258
H	0.000000	-3.856616	1.479998	H	0.000000	-3.827281	1.439416
H	0.000000	3.856616	1.479998	H	0.000000	3.827281	1.439416
CCSD/cc-pVDZ				CCSD/cc-pVTZ			
C	0.000000	1.885640	0.284315	C	0.000000	1.872252	0.277416
C	0.000000	0.675286	-0.456561	C	0.000000	0.666984	-0.442062
C	0.000000	0.000000	-1.737628	C	0.000000	0.000000	-1.700397
C	0.000000	-0.675286	-0.456561	C	0.000000	-0.666984	-0.442062
C	0.000000	-1.885640	0.284315	C	0.000000	-1.872252	0.277416
C	0.000000	-2.934087	0.917337	C	0.000000	-2.908089	0.894567
C	0.000000	2.934087	0.917337	C	0.000000	2.908089	0.894567
H	0.000000	-3.858171	1.473136	H	0.000000	-3.824627	1.432128
H	0.000000	3.858171	1.473136	H	0.000000	3.824627	1.432128
CCSD(T)/cc-pVDZ				CCSD(T)/cc-pVTZ			
C	0.000000	1.885567	0.285145	C	0.000000	1.872781	0.277668
C	0.000000	0.679694	-0.460066	C	0.000000	0.671638	-0.445117
C	0.000000	0.000000	-1.749056	C	0.000000	0.000000	-1.711686
C	0.000000	-0.679694	-0.460066	C	0.000000	-0.671638	-0.445117
C	0.000000	-1.885567	0.285145	C	0.000000	-1.872781	0.277668
C	0.000000	-2.938806	0.924743	C	0.000000	-2.913576	0.902109
C	0.000000	2.938806	0.924743	C	0.000000	2.913576	0.902109
H	0.000000	-3.862132	1.484854	H	0.000000	-3.830371	1.442904
H	0.000000	3.862132	1.484854	H	0.000000	3.830371	1.442904

Table S5: Optimized geometries of the singlet ground electronic state ($\widetilde{X}^1A_1$) of bicyclo[4.1.0]hepta-1,2,4,5-tetraene-7-ylidene (**4**) in Cartesian coordinates (in Ångström units) obtained at different levels within C_{2v} point group symmetry.

MP2/cc-pVDZ				MP2/cc-pVTZ			
C	0.000000	0.000000	-2.095592	C	0.000000	0.000000	-2.064271
C	0.000000	-0.750580	-0.889006	C	0.000000	-0.750634	-0.883033
C	0.000000	0.750580	-0.889006	C	0.000000	0.750634	-0.883033
C	0.000000	-1.435339	0.267959	C	0.000000	-1.417222	0.262953
C	0.000000	1.435339	0.267959	C	0.000000	1.417222	0.262953
C	0.000000	-0.740106	1.463112	C	0.000000	-0.734003	1.448814
C	0.000000	0.740106	1.463112	C	0.000000	0.734003	1.448814
H	0.000000	-1.221192	2.449606	H	0.000000	-1.210722	2.421865
H	0.000000	1.221192	2.449606	H	0.000000	1.210722	2.421865
CCSD/cc-pVDZ				CCSD/cc-pVTZ			
C	0.000000	-0.000000	2.002341	C	0.000000	-0.000000	1.969021
C	0.000000	-0.881192	0.914894	C	0.000000	-0.881519	0.907599
C	-0.000000	0.881192	0.914894	C	-0.000000	0.881519	0.907599
C	0.000000	-1.435952	-0.253116	C	0.000000	-1.418493	-0.247425
C	-0.000000	1.435952	-0.253116	C	-0.000000	1.418493	-0.247425
C	-0.000000	-0.720067	-1.458315	C	-0.000000	-0.712886	-1.442567
C	0.000000	0.720067	-1.458315	C	-0.000000	0.712886	-1.442567
H	-0.000000	-1.218909	-2.436530	H	-0.000000	-1.206254	-2.406577
H	-0.000000	1.218909	-2.436530	H	-0.000000	1.206254	-2.406577
CCSD(T)/cc-pVDZ				CCSD(T)/cc-pVTZ			
C	-0.000000	0.000000	2.040916	C	-0.000000	0.000000	2.003513
C	-0.000000	-0.834848	0.906922	C	-0.000000	-0.842875	0.901951
C	0.000000	0.834848	0.906922	C	0.000000	0.842875	0.901951
C	-0.000000	-1.444199	-0.260130	C	-0.000000	-1.426490	-0.254202
C	0.000000	1.444199	-0.260130	C	0.000000	1.426490	-0.254202
C	-0.000000	-0.730018	-1.461963	C	-0.000000	-0.722380	-1.446681
C	0.000000	0.730018	-1.461963	C	0.000000	0.722380	-1.446681
H	-0.000000	-1.225213	-2.444316	H	-0.000000	-1.212343	-2.414990
H	0.000000	1.225213	-2.444316	H	0.000000	1.212343	-2.414990

Table S6: Optimized geometries of the singlet ground electronic state ($\widetilde{X}^1A_1$) of cyclohepta-1,2,3,4-tetraen-6-yne (**5**) in Cartesian coordinates (in Ångström units) obtained at different levels within C_{2v} point group symmetry.

MP2/cc-pVDZ				MP2/cc-pVTZ			
C	0.000000	0.000000	1.254419	C	0.000000	0.000000	1.246187
C	0.000000	-1.281935	1.003730	C	0.000000	-1.265237	0.990263
C	0.000000	1.281935	1.003730	C	0.000000	1.265237	0.990263
C	0.000000	-1.737047	-0.326698	C	0.000000	-1.721677	-0.326978
C	0.000000	1.737047	-0.326698	C	0.000000	1.721677	-0.326978
C	0.000000	-0.646940	-1.251331	C	0.000000	-0.638095	-1.233800
C	0.000000	0.646940	-1.251331	C	0.000000	0.638095	-1.233800
H	0.000000	-2.789893	-0.629998	H	0.000000	-2.760563	-0.626053
H	0.000000	2.789893	-0.629998	H	0.000000	2.760563	-0.626053
CCSD/cc-pVDZ				CCSD/cc-pVTZ			
C	0.000000	0.000000	1.206904	C	0.000000	0.000000	1.199594
C	0.000000	-1.303070	1.034178	C	0.000000	-1.284178	1.019755
C	0.000000	1.303070	1.034178	C	0.000000	1.284178	1.019755
C	0.000000	-1.717680	-0.347846	C	0.000000	-1.700192	-0.346636
C	0.000000	1.717680	-0.347846	C	0.000000	1.700192	-0.346636
C	0.000000	-0.640515	-1.234920	C	0.000000	-0.630842	-1.218591
C	0.000000	0.640515	-1.234920	C	0.000000	0.630842	-1.218591
H	0.000000	-2.769169	-0.653250	H	0.000000	-2.736987	-0.646831
H	0.000000	2.769169	-0.653250	H	0.000000	2.736987	-0.646831
CCSD(T)/cc-pVDZ				CCSD(T)/cc-pVTZ			
C	0.000000	0.000000	1.221765	C	0.000000	0.000000	1.214925
C	0.000000	-1.306407	1.034815	C	0.000000	-1.287437	1.019854
C	0.000000	1.306407	1.034815	C	0.000000	1.287437	1.019854
C	0.000000	-1.726554	-0.344743	C	0.000000	-1.710069	-0.343935
C	0.000000	1.726554	-0.344743	C	0.000000	1.710069	-0.343935
C	0.000000	-0.646301	-1.246342	C	0.000000	-0.636830	-1.229272
C	0.000000	0.646301	-1.246342	C	0.000000	0.636830	-1.229272
H	0.000000	-2.780210	-0.650253	H	0.000000	-2.749171	-0.644288
H	0.000000	2.780210	-0.650253	H	0.000000	2.749171	-0.644288

Table S7: Optimized geometries of the singlet ground electronic state ($\widetilde{X}^1A'$) of bicyclo[4.1.0]hepta-4,6-diene-2-yne-7-ylidene (**6**) in Cartesian coordinates (in Ångström units) obtained at different levels within C_s point group symmetry.

MP2/cc-pVDZ				MP2/cc-pVTZ			
C	-0.990587	0.672135	0.000000	C	-0.983907	0.677584	0.000000
C	-0.790711	-0.738366	0.000000	C	-0.788986	-0.727469	0.000000
C	0.480960	-1.328131	0.000000	C	0.466938	-1.314420	0.000000
C	1.636882	-0.478983	0.000000	C	1.618698	-0.476716	0.000000
C	1.363794	0.906946	0.000000	C	1.359358	0.899531	0.000000
C	0.180803	1.410027	0.000000	C	0.185369	1.375033	0.000000
C	-2.156940	-0.162807	0.000000	C	-2.128560	-0.155028	0.000000
H	0.650401	-2.409729	0.000000	H	0.628631	-2.383004	0.000000
H	2.633488	-0.933974	0.000000	H	2.599193	-0.933219	0.000000
CCSD/cc-pVDZ				CCSD/cc-pVTZ			
C	-1.008632	0.763199	0.000000	C	-0.999608	0.757114	0.000000
C	-0.830038	-0.653716	0.000000	C	-0.821393	-0.647354	0.000000
C	0.426740	-1.321010	0.000000	C	0.423051	-1.308209	0.000000
C	1.593871	-0.539398	0.000000	C	1.576420	-0.532142	0.000000
C	1.478240	0.915600	0.000000	C	1.459529	0.911538	0.000000
C	0.245544	1.269390	0.000000	C	0.239058	1.248778	0.000000
C	-2.163095	-0.143793	0.000000	C	-2.131603	-0.143319	0.000000
H	0.495729	-2.412733	0.000000	H	0.491186	-2.385067	0.000000
H	2.568730	-1.043492	0.000000	H	2.539653	-1.025121	0.000000
CCSD(T)/cc-pVDZ				CCSD(T)/cc-pVTZ			
C	-1.003983	0.743419	0.000000	C	-0.996662	0.744231	0.000000
C	-0.826937	-0.677796	0.000000	C	-0.820941	-0.669172	0.000000
C	0.436943	-1.328936	0.000000	C	0.429057	-1.315124	0.000000
C	1.608341	-0.531279	0.000000	C	1.589625	-0.525683	0.000000
C	1.460819	0.912370	0.000000	C	1.449613	0.908456	0.000000
C	0.235883	1.314333	0.000000	C	0.232403	1.283343	0.000000
C	-2.172663	-0.142273	0.000000	C	-2.140944	-0.139612	0.000000
H	0.526689	-2.421402	0.000000	H	0.514303	-2.393152	0.000000
H	2.588088	-1.029638	0.000000	H	2.555866	-1.017426	0.000000

Table S8: Optimized geometries of the singlet ground electronic state ($\widetilde{X}^1A_1$) of bicyclo[4.1.0]hepta-1,5-diene-3-yne-7-ylidene (**7**) in Cartesian coordinates (in Ångström units) obtained at different levels within C_{2v} point group symmetry.

MP2/cc-pVDZ				MP2/cc-pVTZ			
C	0.000000	0.000000	-2.105029	C	0.000000	0.000000	-2.078942
C	0.000000	-0.687500	-0.795561	C	0.000000	-0.679816	-0.788374
C	0.000000	0.687500	-0.795561	C	0.000000	0.679816	-0.788374
C	0.000000	-1.534675	0.372660	C	0.000000	-1.520965	0.369951
C	0.000000	1.534675	0.372660	C	0.000000	1.520965	0.369951
C	0.000000	-0.647921	1.442994	C	0.000000	-0.639092	1.425690
C	0.000000	0.647921	1.442994	C	0.000000	0.639092	1.425690
H	0.000000	-2.628021	0.386038	H	0.000000	-2.600004	0.383448
H	0.000000	2.628021	0.386038	H	0.000000	2.600004	0.383448
CCSD/cc-pVDZ				CCSD/cc-pVTZ			
C	0.000000	0.000000	-2.106172	C	0.000000	0.000000	-2.077733
C	0.000000	-0.680851	-0.802007	C	0.000000	-0.672366	-0.794124
C	0.000000	0.680851	-0.802007	C	0.000000	0.672366	-0.794124
C	0.000000	-1.529883	0.382053	C	0.000000	-1.515604	0.379702
C	0.000000	1.529883	0.382053	C	0.000000	1.515604	0.379702
C	0.000000	-0.646850	1.439615	C	0.000000	-0.637366	1.420071
C	0.000000	0.646850	1.439615	C	0.000000	0.637366	1.420071
H	0.000000	-2.622480	0.397993	H	0.000000	-2.592812	0.395523
H	0.000000	2.622480	0.397993	H	0.000000	2.592812	0.395523
CCSD(T)/cc-pVDZ				CCSD(T)/cc-pVTZ			
C	0.000000	0.000000	-2.118499	C	0.000000	0.000000	-2.090120
C	0.000000	-0.684538	-0.804423	C	0.000000	-0.676367	-0.796261
C	0.000000	0.684538	-0.804423	C	0.000000	0.676367	-0.796261
C	0.000000	-1.534542	0.380301	C	0.000000	-1.520871	0.377860
C	0.000000	1.534542	0.380301	C	0.000000	1.520871	0.377860
C	0.000000	-0.652240	1.450135	C	0.000000	-0.642649	1.430454
C	0.000000	0.652240	1.450135	C	0.000000	0.642649	1.430454
H	0.000000	-2.629299	0.395736	H	0.000000	-2.600432	0.393003
H	0.000000	2.629299	0.395736	H	0.000000	2.600432	0.393003

Table S9: Optimized geometries of the singlet ground electronic state ($\widetilde{X}^1A'$) of 1-(buta-1,3-diynyl)propadienylidene (**8**) in Cartesian coordinates (in Ångström units) obtained at different levels within C_s point group symmetry.

MP2/cc-pVDZ				MP2/cc-pVTZ			
C	-1.464248	0.825528	0.000000	C	-1.446928	0.815055	0.000000
C	-2.471594	-0.092592	0.000000	C	-2.443026	-0.095009	0.000000
C	-0.092847	0.472934	0.000000	C	-0.088385	0.470799	0.000000
H	-1.702391	1.902207	0.000000	H	-1.686257	1.877279	0.000000
C	-3.461655	-0.938128	0.000000	C	-3.422104	-0.924348	0.000000
C	1.121832	0.192656	0.000000	C	1.108793	0.189492	0.000000
C	2.456033	-0.134865	0.000000	C	2.428141	-0.133569	0.000000
C	3.660224	-0.427635	0.000000	C	3.614898	-0.423023	0.000000
H	4.705934	-0.686495	0.000000	H	4.646437	-0.679402	0.000000
CCSD/cc-pVDZ				CCSD/cc-pVTZ			
C	-1.469186	0.814728	0.000000	C	-1.451024	0.802273	0.000000
C	-2.478387	-0.083137	0.000000	C	-2.448332	-0.085194	0.000000
C	-0.082967	0.452246	0.000000	C	-0.077750	0.448634	0.000000
H	-1.694975	1.892407	0.000000	H	-1.676651	1.864672	0.000000
C	-3.480472	-0.922920	0.000000	C	-3.439247	-0.906329	0.000000
C	1.118334	0.187733	0.000000	C	1.104175	0.182725	0.000000
C	2.472507	-0.135816	0.000000	C	2.443414	-0.134214	0.000000
C	3.666517	-0.415750	0.000000	C	3.618854	-0.409386	0.000000
H	4.715192	-0.666990	0.000000	H	4.652292	-0.656249	0.000000
CCSD(T)/cc-pVDZ				CCSD(T)/cc-pVTZ			
C	-1.468571	0.822138	0.000000	C	-1.450961	0.810833	0.000000
C	-2.483763	-0.086136	0.000000	C	-2.453225	-0.088525	0.000000
C	-0.086241	0.458645	0.000000	C	-0.081312	0.457755	0.000000
H	-1.695362	1.901986	0.000000	H	-1.679281	1.875280	0.000000
C	-3.488180	-0.930308	0.000000	C	-3.445344	-0.916067	0.000000
C	1.124838	0.191224	0.000000	C	1.110272	0.186050	0.000000
C	2.473039	-0.136750	0.000000	C	2.443526	-0.134951	0.000000
C	3.674538	-0.421624	0.000000	C	3.626633	-0.416461	0.000000
H	4.723732	-0.677852	0.000000	H	4.660883	-0.668318	0.000000

Table S10: Optimized geometries of the singlet ground electronic state ($\widetilde{X}^1A_1$) of heptahexaenylidene (**9**) in Cartesian coordinates (in Ångström units) obtained at different levels within C_{2v} point group symmetry.

MP2/cc-pVDZ				MP2/cc-pVTZ			
C	0.000000	0.000000	-2.482959	C	0.000000	0.000000	-2.451427
C	0.000000	0.000000	-1.199917	C	0.000000	0.000000	-1.184957
C	0.000000	0.000000	-3.823995	C	0.000000	0.000000	-3.778034
H	0.000000	-0.940312	-4.390401	H	0.000000	-0.928874	-4.336636
H	0.000000	0.940312	-4.390401	H	0.000000	0.928874	-4.336636
C	0.000000	0.000000	0.113666	C	0.000000	0.000000	0.113362
C	0.000000	0.000000	1.394833	C	0.000000	0.000000	1.377699
C	0.000000	0.000000	2.716948	C	0.000000	0.000000	2.683996
C	0.000000	0.000000	4.018884	C	0.000000	0.000000	3.967789
CCSD/cc-pVDZ				CCSD/cc-pVTZ			
C	0.000000	0.000000	-2.484704	C	0.000000	0.000000	-2.450408
C	0.000000	0.000000	-1.195977	C	0.000000	0.000000	-1.179767
C	0.000000	0.000000	-3.818424	C	0.000000	0.000000	-3.767666
H	0.000000	-0.941261	-4.382043	H	0.000000	-0.928755	-4.323419
H	0.000000	0.941261	-4.382043	H	0.000000	0.928755	-4.323419
C	0.000000	0.000000	0.110049	C	0.000000	0.000000	0.109593
C	0.000000	0.000000	1.396763	C	0.000000	0.000000	1.377708
C	0.000000	0.000000	2.711073	C	0.000000	0.000000	2.675519
C	0.000000	0.000000	4.017275	C	0.000000	0.000000	3.961228
CCSD(T)/cc-pVDZ				CCSD(T)/cc-pVTZ			
C	0.000000	0.000000	-2.493294	C	0.000000	0.000000	-2.459544
C	0.000000	0.000000	-1.202198	C	0.000000	0.000000	-1.186077
C	0.000000	0.000000	-3.837263	C	0.000000	0.000000	-3.787248
H	0.000000	-0.942723	-4.402408	H	0.000000	-0.930552	-4.344390
H	0.000000	0.942723	-4.402408	H	0.000000	0.930552	-4.344390
C	0.000000	0.000000	0.111320	C	0.000000	0.000000	0.110780
C	0.000000	0.000000	1.401790	C	0.000000	0.000000	1.383226
C	0.000000	0.000000	2.722661	C	0.000000	0.000000	2.687385
C	0.000000	0.000000	4.036460	C	0.000000	0.000000	3.981209

Table S11: Computed energies of C_7H_2 isomers in their ground electronic states calculated at RHF-fc-MP2/cc-pVDZ level of theory.

Isomer[a]	Point Group	E a.u	$ZPVE$ kcal mol^{-1}	E+$ZPVE$ a.u	μ Debye	ΔE kcal mol^{-1}	ΔE+$ZPVE$ kcal mol^{-1}	Rank ΔE	Rank ΔE+$ZPVE$
1	$D_{\infty h}$	-266.85552570	40.6208	-266.79079239	-	0.0000	0.0000	1	2
2	C_s	-266.83864323	32.3079	-266.78715736	3.7493	10.5939	2.2810	4	3
3	C_{2v}	-266.83357952	31.9058	-266.78273444	3.9003	13.7714	5.0564	5	5
4	C_{2v}	-266.85389606	35.6681	-266.79705538	3.6056	1.0226	-3.9301	2	1
5	C_{2v}	-266.84050428	34.8900	-266.78490358	1.2757	9.4261	3.6953	3	4
6	C_s	-266.82504925	34.9563	-266.76934289	3.9712	19.1243	13.4598	6	6
7	C_{2v}	-266.82289381	34.4526	-266.76799015	3.0132	20.4768	14.3086	7	7
8	C_s	-266.80989257	31.6779	-266.75941067	5.7711	28.6352	19.6923	8	8
9	C_{2v}	-266.80345955	32.0377	-266.75240427	7.7824	32.6720	24.0889	9	9

[a] For isomer **1** the calculation is done using a ROHF wave function since the electronic state is a triplet.

Table S12: Computed energies of C_7H_2 isomers in their ground electronic states calculated at RHF-fc-CCSD/cc-pVDZ level of theory.

Isomer[a]	Point Group	E a.u	$ZPVE$ kcal mol^{-1}	E+$ZPVE$ a.u	μ Debye	ΔE kcal mol^{-1}	ΔE+$ZPVE$ kcal mol^{-1}	Rank ΔE	Rank ΔE+$ZPVE$
1	$D_{\infty h}$	-266.86579631	29.6736	-266.81850846	-	0.0000	0.0000	1	1
2	C_s	-266.86399942	32.7009	-266.81188727	3.5784	1.1276	4.1549	2	2
3	C_{2v}	-266.86081907	32.3511	-266.80926436	3.7086	3.1233	5.8008	3	3
4	C_{2v}	-266.85003393	34.5181	-266.79502589	3.3789	9.8910	14.7355	4	4
5	C_{2v}	-266.84682009	34.6623	-266.79158225	2.1068	11.9078	16.8965	5	5
6	C_s	-266.84036319	34.3815	-266.78557283	2.7739	15.9595	20.6674	8	7
7	C_{2v}	-266.84098881	34.7966	-266.78553695	3.0077	15.5669	20.6899	7	8
8	C_s	-266.84118025	32.1151	-266.79000163	4.7239	15.4468	17.8883	6	6
9	C_{2v}	-266.83179006	32.0354	-266.78073845	6.9566	21.3392	23.7010	9	9

[a] For isomer **1** the calculation is done using a ROHF wave function since the electronic state is a triplet.

Table S13: Computed energies of C_7H_2 isomers in their ground electronic states calculated at RHF-fc-CCSD(T)/cc-pVDZ level of theory.

Isomer[a]	Point Group	E a.u	$ZPVE$ kcal mol^{-1}	E+$ZPVE$ a.u	μ Debye	ΔE kcal mol^{-1}	ΔE+$ZPVE$ kcal mol^{-1}	Rank ΔE	Rank ΔE+$ZPVE$
1	$D_{\infty h}$	-266.91536735	30.2626	-266.86714087	-	0.0000	0.0000	1	1
2	C_s	-266.91005014	31.8783	-266.85924888	3.5812	3.3366	4.9523	2	2
3	C_{2v}	-266.90633926	31.5176	-266.85611281	3.7070	5.6652	6.9202	5	3
4	C_{2v}	-266.90942489	33.8440	-266.85549109	3.2715	3.7289	7.3103	3	4
5	C_{2v}	-266.90729021	34.0102	-266.85309156	1.7767	5.0685	8.8161	4	5
6	C_s	-266.89512778	33.7630	-266.84132306	2.9631	12.7005	16.2009	7	6
7	C_{2v}	-266.89546265	33.9771	-266.84131674	2.9491	12.4904	16.2049	6	7
8	C_s	-266.89016128	31.2700	-266.84032941	4.9904	15.8170	16.8244	8	8
9	C_{2v}	-266.88836830	31.2632	-266.83854726	6.9538	16.9422	17.9428	9	9

[a] For isomer **1** the calculation is done using a ROHF wave function since the electronic state is a triplet.

Table S14: Computed energies of C_7H_2 isomers in their ground electronic states calculated at RHF-fc-MP2/cc-pVTZ level of theory.

Isomer[a]	Point Group	E a.u	$ZPVE$ kcal mol^{-1}	E+$ZPVE$ a.u	μ Debye	ΔE kcal mol^{-1}	ΔE+$ZPVE$ kcal mol^{-1}	Rank ΔE	Rank ΔE+$ZPVE$
1	$D_{\infty h}$	-267.09794881	39.1010	-267.03563746	-	0.0000	0.0000	1	1
2	C_s	-267.07894921	32.3955	-267.02732374	3.8067	11.9224	5.2169	4	3
3	C_{2v}	-267.07366888	32.0594	-267.02257902	3.9328	15.2359	8.1943	5	5
4	C_{2v}	-267.08982681	35.6420	-267.03302772	3.6311	5.0966	1.6376	2	2
5	C_{2v}	-267.07944544	35.0475	-267.02359374	1.4087	11.6110	7.5575	3	4
6	C_s	-267.06166274	34.8872	-267.00606650	3.8990	22.7699	18.5561	6	6
7	C_{2v}	-267.05936398	34.6330	-267.00417283	3.1035	24.2123	19.7444	7	7
8	C_s	-267.04776153	31.9011	-266.99692394	5.9955	31.4930	24.2931	8	8
9	C_{2v}	-267.04239025	31.8948	-266.99156270	8.0930	34.8635	27.6573	9	9

[a] For isomer **1** the calculation is done using a ROHF wave function since the electronic state is a triplet.

Table S15: Computed energies of C_7H_2 isomers in their ground electronic states calculated at RHF-fc-CCSD/cc-pVTZ level of theory.

Isomer[a]	Point Group	E a.u	$ZPVE$ kcal mol^{-1}	E+$ZPVE$ a.u	μ Debye	ΔE kcal mol^{-1}	ΔE+$ZPVE$ kcal mol^{-1}	Rank ΔE	Rank ΔE+$ZPVE$
1	$D_{\infty h}$	-267.09224754	30.0345	-267.04438456	-	0.0000	0.0000	1	1
2	C_s	-267.09009770	33.0309	-267.03745966	3.6727	1.3490	4.3454	2	2
3	C_{2v}	-267.08682701	32.7415	-267.03465016	3.7814	3.4014	6.1084	3	3
4	C_{2v}	-267.07080970	34.8729	-267.01523625	3.4526	13.4524	18.2908	4	4
5	C_{2v}	-267.06808274	34.9870	-267.01232746	2.2080	15.1636	20.1161	5	6
6	C_s	-267.06094370	34.7573	-267.00555447	2.8272	19.6435	24.3662	7	7
7	C_{2v}	-267.06067152	35.1482	-267.00465935	3.1201	19.8143	24.9279	8	8
8	C_s	-267.06392613	31.5399	-267.01366415	4.9784	17.7720	19.2773	6	5
9	C_{2v}	-267.05434324	32.1444	-267.00311792	7.3629	23.7853	25.8952	9	9

[a] For isomer **1** the calculation is done using a ROHF wave function since the electronic state is a triplet.

Table S16: Computed energies of C_7H_2 isomers in their ground electronic states calculated at RHF-fc-CCSD(T)/cc-pVTZ level of theory.

Isomer[a]	Point Group	E a.u	$ZPVE$ kcal mol^{-1}	E+$ZPVE$ a.u	μ Debye	ΔE kcal mol^{-1}	ΔE+$ZPVE$ kcal mol^{-1}	Rank ΔE	Rank ΔE+$ZPVE$
1	$D_{\infty h}$	-267.15902785	30.3810	-267.11061269	-	0.0000	0.0000	1	1
2	C_s	-267.15263089	32.1976	-267.10132079	3.6703	4.0141	5.8308	2	2
3	C_{2v}	-267.14875699	31.9086	-267.09790745	3.7740	6.4451	7.9727	3	3
4	C_{2v}	-267.14683795	34.1635	-267.09239495	3.3567	7.6493	11.4318	4	4
5	C_{2v}	-267.14572965	34.3097	-267.09105371	1.8778	8.3447	12.2734	5	5
6	C_s	-267.13248509	34.0798	-267.07817552	2.9636	16.6558	20.3546	6	7
7	C_{2v}	-267.13205626	34.3065	-267.07738542	3.0677	16.9249	20.8504	7	9
8	C_s	-267.12961328	31.7172	-267.07906875	5.2467	18.4579	19.7941	8	6
9	C_{2v}	-267.12771931	31.3582	-267.07774688	7.3360	19.6464	20.6236	9	8

[a] For isomer **1** the calculation is done using a ROHF wave function since the electronic state is a triplet.

Table S17: Relative energies of C_7H_2 isomers without and with ZPVE correction (in parentheses) calculated at different levels of theory. All values are in kcal mol^{-1}.

Isomer	Electronic State	Symmetry	cc-pVDZ			cc-pVTZ		
			MP2	CCSD	CCSD(T)	MP2	CCSD	CCSD(T)
1	$\widetilde{X}^3\Sigma_g^-$	$D_{\infty h}$	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)
2	$\widetilde{X}^1\mathrm{A}'$	C_s	10.59 (2.28)	1.13 (4.16)	3.34 (4.95)	11.92 (5.22)	1.35 (4.35)	4.01 (5.83)
3	$\widetilde{X}^1\mathrm{A}_1$	C_{2v}	13.77 (5.06)	3.12 (5.80)	5.67 (6.92)	15.24 (8.19)	3.40 (6.11)	6.45 (7.97)
4	$\widetilde{X}^1\mathrm{A}_1$	C_{2v}	1.02 (-3.93)	9.89 (14.74)	3.73 (7.31)	5.10 (1.64)	13.45 (18.29)	7.65 (11.43)
5	$\widetilde{X}^1\mathrm{A}_1$	C_{2v}	9.43 (3.70)	11.91 (16.90)	5.07 (8.82)	11.61 (7.56)	15.16 (20.12)	8.35 (12.27)
6	$\widetilde{X}^1\mathrm{A}'$	C_s	19.12 (13.46)	15.96 (20.67)	12.70 (16.20)	22.77 (18.56)	19.64 (24.37)	16.66 (20.36)
7	$\widetilde{X}^1\mathrm{A}_1$	C_{2v}	20.48 (14.31)	15.57 (20.69)	12.49 (16.21)	24.21 (19.74)	19.81 (24.93)	16.93 (20.85)
8	$\widetilde{X}^1\mathrm{A}'$	C_s	28.64 (19.69)	15.45 (17.89)	15.82 (16.82)	31.49 (24.29)	17.77 (19.28)	18.46 (19.79)
9	$\widetilde{X}^1\mathrm{A}_1$	C_{2v}	32.67 (24.09)	21.34 (23.70)	16.94 (17.94)	34.86 (27.66)	23.79 (25.90)	19.65 (20.62)

Table S18: Isotopic shifts (^{12}C $-^{13}$C) in harmonic vibrational frequencies (cm^{-1}) for isomers **1**, **2**, and **3** computed at the CCSD(T)/cc-pVTZ level of theory.

Mode	Isomer **1**[a]				Isomer **2**							Isomer **3**			
	C(1)	C(2)	C(4)	C(6)	C(1)	C(2)	C(3)	C(4)	C(5)	C(7)	C(8)	C(1)	C(2)	C(3)	C(7)
1	1	0	0	1	0	1	1	0	1	0	1	0	0	0	1
2	0	2	0	1	0	1	1	0	1	0	0	1	1	2	1
3	6	0	4	1	1	1	3	2	1	1	1	2	1	1	1
4	4	4	2	1	2	2	2	3	1	0	0	2	1	0	1
5	0	2	4	1	1	2	4	9	1	0	1	7	0	1	1
6	0	0	0	2	7	1	5	6	0	0	1	4	4	1	0
7	0	0	0	0	2	8	3	2	1	0	4	4	2	8	1
8	0	1	4	6	2	1	1	4	4	5	2	0	0	0	3
9	11	7	2	6	4	6	5	3	0	0	0	0	0	1	1
10	0	26	1	6	0	0	0	0	4	0	0	3	8	0	1
11	1	2	26	11	0	0	0	0	5	0	0	3	2	5	5
12	0	6	19	7	3	0	0	0	0	9	0	0	1	0	4
13	55	15	1	1	3	2	1	1	2	2	6	0	0	0	1
14	0	0	0	13	10	4	3	1	3	7	5	2	8	5	3
15	0	0	0	3	8	9	9	1	4	12	3	0	20	3	3
16					7	0	0	0	0	14	25	0	11	26	0
17					38	0	4	0	1	17	3	1	29	3	3
18					1	16	4	41	21	0	0	46	1	0	19
19					1	28	38	11	3	0	0	4	3	0	4
20					0	0	0	0	0	13	0	1	0	0	15
21					0	0	0	1	17	0	0	1	0	0	2

[a] At the ROCCSD(T)/cc-pVTZ level of theory since the ground electronic state is a triplet.

Table S19: Isotopic shifts (^{12}C $-^{13}$C) in harmonic vibrational frequencies (cm^{-1}) for isomers **4**, **5**, and **6** computed at the CCSD(T)/cc-pVTZ level of theory.

Mode	Isomer **4**				Isomer **5**				Isomer **6**						
	C(1)	C(2)	C(4)	C(6)	C(1)	C(2)	C(4)	C(6)	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)
1	5	1	1	1	2	0	2	1	1	1	0	0	1	1	3
2	3	6	0	0	0	4	1	1	3	0	0	0	2	6	1
3	0	3	0	3	1	4	1	2	3	2	1	3	5	0	0
4	1	7	2	1	0	2	1	8	5	2	2	0	1	8	1
5	1	1	6	2	0	0	1	9	2	6	0	2	4	2	4
6	1	4	5	1	9	4	1	0	4	8	4	3	1	1	0
7	0	5	4	2	11	1	2	3	2	0	4	8	3	3	6
8	1	0	5	9	7	4	3	2	2	3	5	1	3	5	13
9	0	0	0	4	0	1	9	0	0	2	5	2	0	0	0
10	17	1	5	2	1	0	1	0	1	3	16	1	6	0	7
11	8	1	5	7	0	2	10	3	0	0	3	7	0	0	0
12	0	0	0	6	2	7	8	2	14	16	1	2	1	4	1
13	8	0	2	6	5	8	11	0	1	1	3	11	7	3	2
14	4	5	5	2	0	0	5	9	2	0	3	10	3	2	1
15	6	3	7	4	0	3	8	0	5	11	2	8	5	1	2
16	0	1	3	17	0	0	9	5	1	2	22	16	0	0	0
17	1	3	2	11	1	20	2	0	15	7	5	2	8	2	1
18	1	25	22	2	45	11	0	0	14	23	4	2	4	1	11
19	6	9	6	0	0	0	2	34	7	1	0	0	20	40	1
20	0	0	0	6	0	0	10	0	0	0	1	10	0	0	0
21	0	0	0	4	0	0	0	0	0	0	10	1	0	0	0

Table S20: Isotopic shifts ($^{12}C - ^{13}C$) in harmonic vibrational frequencies (cm^{-1}) for isomers **7**, **8**, and **9** computed at the CCSD(T)/cc-pVTZ level of theory.

Mode	Isomer **7**				Isomer **8**							Isomer **9**						
	C(1)	C(2)	C(4)	C(6)	C(1)	C(2)	C(3)	C(5)	C(6)	C(7)	C(8)	C(1)	C(2)	C(3)	C(6)	C(7)	C(8)	C(9)
1	2	1	0	1	0	0	1	1	0	0	1	0	0	1	1	0	0	1
2	0	2	2	1	1	0	1	0	2	0	1	0	0	1	1	0	0	1
3	5	3	0	3	1	1	0	1	2	1	1	1	1	1	0	1	2	1
4	5	0	1	6	0	5	0	2	0	0	0	1	1	1	0	1	2	1
5	0	2	0	8	0	4	4	1	1	2	0	4	1	0	2	0	1	0
6	4	2	4	4	0	0	6	0	1	4	1	3	1	1	4	1	3	0
7	0	9	3	1	0	2	0	1	6	8	1	1	9	0	5	0	1	0
8	0	1	5	1	1	4	5	2	9	7	2	0	0	0	1	10	6	0
9	8	1	11	0	0	0	2	0	3	3	1	8	8	0	0	4	1	0
10	0	5	3	0	0	0	0	0	0	0	4	3	1	6	0	1	4	6
11	2	4	6	0	0	0	0	0	0	0	5	1	3	0	7	9	2	0
12	2	0	7	6	13	2	5	0	0	3	5	1	0	8	0	0	0	0
13	1	9	1	1	12	1	2	0	0	0	0	4	0	8	0	0	0	0
14	12	10	3	2	14	1	4	13	3	1	2	0	5	9	11	5	1	10
15	1	10	7	1	5	0	8	1	9	0	3	6	4	0	1	6	1	4
16	4	4	7	1	23	1	2	5	3	0	1	4	10	16	0	9	2	5
17	0	0	13	12	9	50	0	17	0	0	0	19	0	4	18	1	27	11
18	3	24	0	4	1	0	18	0	7	39	21	21	36	1	22	14	2	0
19	0	4	2	28	0	0	25	0	37	12	3	3	0	1	6	22	20	4
20	0	0	10	0	10	0	0	0	0	0	0	0	0	6	0	0	0	0
21	0	0	1	0	0	0	0	0	0	1	17	0	0	13	0	0	0	0