Structure and Bonding Patterns in C_5H_4 isomers: Pyramidane, Planar Tetracoordinate Carbon, and Spiro molecules

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Table S1: Optimized geometries of the C_5H_4 isomers in singlet ground electronic state in Cartesian coordinates (in Angstrom units) obtained at CCSD(T)/cc-pVTZ level of theory:

	py-1				**py-2**		
C	0.000356681	-0.004248912	-1.049041058	C	-1.163495180	-0.127721035	0.197087399
C	-0.085440477	1.024427177	0.251312710	C	0.047321236	-1.014789595	0.250938138
C	1.023348862	0.086363875	0.253305893	C	1.011900980	0.113275068	0.328882708
C	0.085278607	-1.022429459	0.255295288	C	0.094601133	0.009182151	-0.902977469
C	-1.023523295	-0.084355531	0.253302078	C	-0.177311791	0.999367623	0.249646448
H	-0.173988082	2.085988114	0.102582438	H	-0.273712603	2.063337771	0.097620634
H	2.085206773	0.174650474	0.106635756	H	0.224330767	0.023155569	-1.966582294
H	0.173873425	-2.084536183	0.110703748	H	2.087163977	0.233735972	0.296799781
H	-2.085334834	-0.173210810	0.106641196	H	0.188599893	-2.073927148	0.100749019
	ptC-1				**ptC-2**		
C	1.371675992	-0.679675925	0.003506207	C	-1.232294086	0.743993758	0.000000000
C	-0.000714839	-0.000293963	-0.027737349	C	0.091724124	-0.000320988	0.000000000
C	-1.372823931	0.679656547	0.003512287	C	1.427355472	-0.676024444	0.000000000
C	-1.368950306	-0.680756712	0.003479213	C	1.430777455	0.675152545	0.000000000
C	1.370705248	0.681046955	0.003473096	C	-1.232896697	-0.742941844	0.000000000
H	2.106231286	1.497984690	0.040928987	H	-1.442673486	1.283737237	-0.914676726
H	2.108366892	-1.495561551	0.041001833	H	-1.442745597	-1.282897936	-0.914683277
H	-2.109176565	1.495848344	0.040989202	H	-1.442745597	-1.282897936	0.914683277
H	-2.104137639	-1.497996480	0.040995885	H	-1.442673486	1.283737237	0.914676726
	ptC-3				**spiro-1**		
C	-1.548117694	0.465503547	0.000000000	C	0.000000000	0.000000000	0.000000000
C	-1.111517788	-0.916164291	0.000000000	C	0.000000000	0.662034000	1.330054000
C	0.001236476	0.002205187	0.000000000	C	0.000000000	-0.662034000	1.330054000
C	1.113301295	0.916118332	0.000000000	C	-0.662034000	0.000000000	-1.330054000
C	1.545744123	-0.467206799	0.000000000	C	0.662034000	0.000000000	-1.330054000
H	1.874306472	-0.946005802	-0.919418990	H	0.000000000	1.560710000	1.927681000
H	1.874306472	-0.946005802	0.919418990	H	0.000000000	-1.560710000	1.927681000
H	-1.878154797	0.943291171	0.919424171	H	-1.560710000	0.000000000	-1.927681000
H	-1.878154797	0.943291171	-0.919424171	H	1.560710000	0.000000000	-1.927681000
	spiro-2				**spiro-3**		
C	0.000000000	0.772810000	-1.122997000	C	1.058484000	-0.830035000	-0.383540000
C	0.000000000	-0.772810000	-1.123008000	C	-0.051275000	-1.390634000	0.433504000
C	0.000000000	-0.000002000	0.129611000	C	-0.000006000	-0.000005000	0.430910000
C	-0.630863000	0.000006000	1.521221000	C	0.051282000	1.390624000	0.433496000
C	0.630863000	0.000002000	1.521222000	C	-1.058483000	0.830036000	-0.383549000
H	0.916542000	-1.282713000	-1.392977000	H	-0.992647000	0.713468000	-1.462267000
H	-0.916542000	1.282710000	-1.392973000	H	-2.060628000	0.842751000	0.039498000
H	0.916541000	1.282710000	-1.392973000	H	2.060633000	-0.842737000	0.039497000
H	-0.916541000	-1.282713000	-1.392977000	H	0.992642000	-0.713469000	-1.462259000
	spiro-4		
C	0.468583000	1.435715000	0.000003000
C	-1.065840000	1.069288000	0.000000000
C	0.017646000	0.077939000	0.000001000
C	0.458026000	-1.223288000	0.645956000
C	0.458024000	-1.223288000	-0.645955000
H	0.583969000	-1.684856000	-1.607789000
H	-1.600776000	1.314885000	0.912940000
H	0.583974000	-1.684858000	1.607788000
H	-1.600772000	1.314883000	-0.912943000

Table S2: Optimized geometries of the C_5H_4 isomers in triplet ground electronic state and quintet electronic state for **ptC-1** in Cartesian coordinates (in Angstrom units) obtained at B3LYP/6-311+G(d,p) level of theory.

py-1

C	0.000000000	0.000000000	0.855123000
C	0.000000000	1.100891000	-0.235013000
C	-1.100891000	0.000000000	-0.235013000
C	0.000000000	-1.100891000	-0.235013000
C	1.100891000	0.000000000	-0.235013000
H	0.000000000	2.117265000	0.127394000
H	-2.117265000	0.000000000	0.127394000
H	0.000000000	-2.117265000	0.127394000
H	2.117265000	0.000000000	0.127394000

py-2

C	-0.856875000	-1.046206000	0.000000000
C	-0.135923000	-0.165956000	1.003958000
C	-0.135923000	-0.165956000	-1.003958000
C	-0.135923000	0.988980000	0.000000000
C	0.996443000	0.061606000	0.000000000
H	2.074730000	0.116628000	0.000000000
H	-0.085293000	-0.104158000	-2.081224000
H	-0.294940000	2.056879000	0.000000000
H	-0.085293000	-0.104158000	2.081224000

ptC-1

C	1.305853000	0.687489000	0.050490000
C	1.305853000	-0.687489000	0.050490000
C	0.000000000	0.000000000	0.195312000
C	-1.305853000	0.687489000	0.050490000
C	-1.305853000	-0.687489000	0.050490000
H	-1.545152000	1.529971000	-0.595910000
H	-1.545152000	-1.529971000	-0.595910000
H	1.545152000	1.529971000	-0.595910000
H	1.545152000	-1.529971000	-0.595910000

ptC-2

C	0.000000000	0.647220000	1.607238000
C	0.000000000	-0.647220000	1.607238000
C	0.000000000	0.000000000	0.092284000
C	0.000000000	0.764571000	-1.165173000
C	0.000000000	-0.764571000	-1.165173000
H	-0.914591000	-1.277921000	-1.464618000
H	0.914591000	-1.277921000	-1.464618000
H	0.914591000	1.277921000	-1.464618000
H	-0.914591000	1.277921000	-1.464618000

ptC-3

C	0.000000000	2.612392000	0.000000000
C	0.000190000	1.280911000	0.000000000
C	0.000000000	0.000000000	0.000000000
C	-0.000190000	-1.280911000	0.000000000
C	0.000000000	-2.612392000	0.000000000
H	-0.001387000	-3.181842000	0.926998000
H	-0.001387000	-3.181842000	-0.926998000
H	0.001387000	3.181842000	-0.926998000
H	0.001387000	3.181842000	0.926998000

spiro-1

C	0.000000000	0.656823000	1.328726000
C	0.000000000	-0.656823000	1.328726000
C	0.000000000	0.000000000	0.000000000
C	0.656823000	0.000000000	-1.328726000
C	-0.656823000	0.000000000	-1.328726000
H	1.554201000	0.000000000	-1.931125000
H	-1.554201000	0.000000000	-1.931125000
H	0.000000000	-1.554201000	1.931125000
H	0.000000000	1.554201000	1.931125000

spiro-2

C	0.000000000	0.778720000	-1.115910000
C	0.000000000	-0.778720000	-1.115910000
C	0.000000000	0.000000000	0.128735000
C	-0.649890000	0.000000000	1.526417000
C	0.649890000	0.000000000	1.526417000
H	0.912693000	-1.280751000	-1.424623000
H	-0.912693000	1.280751000	-1.424623000
H	0.912693000	1.280751000	-1.424623000
H	-0.912693000	-1.280751000	-1.424623000

spiro-3

C	1.509330000	-1.240533000	-0.258740000
C	0.122093000	-1.321370000	-0.167665000
C	0.000000000	0.000000000	-0.258740000
C	-0.122093000	1.321370000	-0.167665000
C	-1.509330000	1.240533000	-0.258740000
H	-1.989290000	1.392116000	-1.225354000
H	-2.142478000	1.129390000	0.622775000
H	2.142478000	-1.129390000	0.622775000
H	1.989290000	-1.392116000	-1.225354000

spiro-4

C	0.402742000	1.452771000	0.000000000
C	-1.029778000	1.155894000	0.000000000
C	0.170355000	0.053751000	0.000000000
C	0.402742000	-1.239088000	0.655544000
C	0.402742000	-1.239088000	-0.655544000
H	0.570690000	-1.777828000	-1.575134000
H	-1.617095000	1.225109000	0.917834000
H	0.570690000	-1.777828000	1.575134000
H	-1.617095000	1.225109000	-0.917834000

ptC-1 (quintet state)

C	1.217274000	0.701947000	-0.032499000
C	1.217274000	-0.701947000	-0.032499000
C	0.000000000	0.000000000	0.661047000
C	-1.217274000	0.701947000	-0.032499000
C	-1.217274000	-0.701947000	-0.032499000
H	-1.198875000	1.474159000	-0.796629000
H	-1.198875000	-1.474159000	-0.796629000
H	1.198875000	1.474159000	-0.796629000
H	1.198875000	-1.474159000	-0.796629000

Table S3: Dipole moments in different axis (in Debye), total dipole moment ($|\mu|$ in Debye), Centrifugal distortion constants, and rotational constants (in MHz) of C_5H_4 isomers in their ground electronic states calculated at the CCSD(T)/cc-pVTZ level of theory.

Isomer	μ_a	μ_b	μ_c	$|\mu|$	D_J	D_K	D_{JK}	d_1	d_2	A_e	B_e	C_e
Pent-1,2-diyne	0.00	0.00	1.36	1.36	---	---	---	---	---	159960.54	2014.97	2014.97
py-1	0.00	0.01	1.82	1.83	5.20×10^{-3}	3.27×10^{-3}	-4.72×10^{-3}	6.92×10^{-4}	1.42×10^{-3}	10013.43	10013.39	7401.87
py-2	3.93	0.44	1.21	4.26	3.98×10^{-3}	1.84×10^{-3}	-2.80×10^{-3}	-6.43×10^{-4}	6.53×10^{-4}	10020.89	9977.03	7546.34
ptc-1	0.02	0.01	0.28	0.57	6.28×10^{-4}	-2.47×10^{-2}	3.47×10^{-2}	-1.61×10^{-4}	-2.45×10^{-5}	16165.57	4673.34	3626.16
ptc-2	4.64	0.00	0.00	4.64	1.12×10^{-3}	5.70×10^{-3}	1.53×10^{-3}	-2.11×10^{-4}	9.83×10^{-5}	14763.42	5191.84	4048.62
ptc-3	0.00	0.00	0.00	0.00	2.53×10^{-4}	2.21×10^{-4}	3.22×10^{-2}	-3.01×10^{-5}	1.82×10^{-4}	15768.47	3909.69	4856.63
spiro-1	0.00	0.00	0.00	0.00	---	---	---	---	---	16366.78	4378.85	4378.85
spiro-2	3.40	0.00	0.00	3.40	---	---	---	---	---	14895.47	4750.50	4416.97
spiro-3	0.00	0.00	2.46	2.61	---	---	---	---	---	13353.51	5379.75	4907.22
spiro-4	2.59	2.09	0.00	3.57	---	---	---	---	---	14705.66	4582.37	4560.19

Table S4: The energy gap between singlet and triplet spin state (ΔE_{st} in kcal mol^{-1}), number of imaginary frequencies (NImag), and dipole moment ($|\mu|$ in Debye) of all nine isomers of C_5H_4 at B3LYP/6-311+G(d,p) level of theory.

Molecules	ΔE_{st}	NImag	$|\mu|$
py-1	111.71	3	1.81
Py-2	36.07	0	2.64
ptC-1	1.79	2	2.59
ptC-2	57.16	3	2.2
ptC-3	-110.56	0	0
spiro-1	59.64	2	1.58
spiro-2	15.39	0	1.84
spiro-3	-88.68	0	0
spiro-4	9.41	0	3.06

Table S5: The energy gap between singlet and triplet spin state (ΔE_{st} in kcal mol^{-1}), number of imaginary frequencies (NImag), and dipole moment ($|\mu|$ in Debye) of all nine isomers of C_5H_4 at ωB97XD/6-311+G(d,p) level of theory.

Molecules	ΔE_{st}	NImag	$|\mu|$
py-1	147.78	2	2.79
Py-2	36.87	0	2.18
ptC-1	1.51	2	0.00
ptC-2	60.69	3	7.38
ptC-3	-4.40	2	2.53
spiro-1	61.54	2	1.73
spiro-2	15.01	0	1.75
spiro-3	17.89	1	1.09
spiro-4	10.03	0	2.99

Table S6: Electron density descriptors (in a.u.) at the (3, –1) bond critical points (BCP) obtained from the B3LYP/6-311+G(d,p) level for all the nine isomers. The topological parameters such as Hamiltionian Kinetic Energy K(r_c), $\rho(r_c)$, Laplacian Electron Density ($\nabla^2\rho(r_c)$), Lagrangian Kinetic Energy G(r_c), Potential Energy Density V(r_c), Energy Density E(r_c) or H(r_c), ELF, G(r_c)/V(r_c), and G(r_c)/$\rho(r_c)$ at the critical points are also given.

Molecules	BCP	Index	K(r_c)	$\rho(r_c)$	($\nabla^2\rho(r_c)$)	G(r_c)	V(r_c)	H(r_c)	ELF	G(r_c)/V(r_c)	G(r_c) / $\rho(r_c)$
py-1	8(H)-- 4(C)	10	0.284	0.285	-1.000	0.034	-0.318	-0.284	0.99	-0.107	0.120
	4(C)--1(C)	11	0.104	0.169	-0.016	0.100	-0.205	-0.104	0.69	-0.490	0.594
	4(C)--3(C)	12	0.251	0.271	-0.614	0.097	-0.348	-0.251	0.92	-0.280	0.359
py-2	9(H)--2(C)	10	0.281	0.283	-0.988	0.034	-0.315	-0.281	0.99	-0.108	0.121
	2(C)--4(C)	11	0.218	0.252	-0.499	0.093	-0.311	-0.218	0.91	-0.300	0.370
	2(C)--1(C)	12	0.226	0.252	-0.532	0.093	-0.318	-0.226	0.91	-0.291	0.367
ptC-1	7(H)--5(C)	10	0.250	0.264	-0.856	0.036	-0.286	-0.250	0.99	-0.125	0.135
	5(C)--3(C)	12	0.175	0.225	-0.236	0.116	-0.291	-0.175	0.81	-0.399	0.515
	5(C)--4(C)	14	0.361	0.325	-0.887	0.139	-0.499	-0.361	0.91	-0.278	0.427
ptC-2	6(H)--5(C)	10	0.277	0.280	-0.956	0.038	-0.315	-0.277	0.99	-0.120	0.135
	2(C)--1(C)	12	0.428	0.357	-0.110	0.153	-0.581	-0.428	0.92	-0.263	0.427
	2(C)--3(C)	13	0.165	0.230	0.059	0.179	-0.344	-0.165	0.66	-0.521	0.779
	5(C)--3(C)	14	0.181	0.227	-0.352	0.093	-0.275	-0.181	0.87	-0.340	0.412
	5(C)--4(C)	16	0.214	0.250	-0.506	0.088	-0.302	-0.214	0.91	-0.291	0.351
ptC-3	6(H)--5(C)	10	0.272	0.277	-0.940	0.037	-0.309	-0.272	0.99	-0.119	0.133
	5(C)--4(C)	12	0.274	0.283	-0.687	0.102	-0.377	-0.274	0.92	-0.272	0.362
	4(C)--3(C)	13	0.239	0.253	-0.446	0.128	-0.367	-0.239	0.84	-0.348	0.505
spiro-1	8(H)--2(C)	10	0.273	0.277	-0.946	0.036	-0.309	-0.273	0.99	-0.118	0.132
	2(C)--3(C)	11	0.201	0.242	-0.368	0.109	-0.310	-0.201	0.86	-0.351	0.449
	2(C)--1(C)	12	0.398	0.340	-0.899	0.173	-0.571	-0.398	0.88	-0.303	0.511
spiro-2	9(H)--2(C)	10	0.271	0.276	-0.924	0.040	-0.311	-0.271	0.99	-0.129	0.145
	4(C)--5(C)	12	0.591	0.421	-1.457	0.227	-0.818	-0.591	0.90	-0.278	0.540
	2(C)--3(C)	13	0.239	0.264	-0.568	0.097	-0.336	-0.239	0.91	-0.288	0.366
	2(C)--1(C)	15	0.166	0.220	-0.319	0.086	-0.252	-0.166	0.88	-0.342	0.392
spiro-3	2(C)--1(C)	10	0.235	0.260	-0.523	0.104	-0.339	-0.235	0.90	-0.307	0.400
	2(C)--3(C)	11	0.285	0.277	-0.589	0.138	-0.423	-0.285	0.86	-0.326	0.496
	1(C)--8(H)	12	0.270	0.277	-0.935	0.036	-0.306	-0.270	0.99	-0.119	0.131
spiro-4	8(H)--4(C)	10	0.281	0.282	-0.991	0.033	-0.314	-0.281	0.99	-0.106	0.118
	4(C)--5(C)	11	0.452	0.362	-1.016	0.198	-0.650	-0.452	0.88	-0.305	0.548
	4(C)--3(C)	13	0.165	0.218	-0.217	0.110	-0.275	-0.165	0.81	-0.401	0.505
	3(C)--2(C)	15	0.216	0.251	-0.455	0.103	-0.319	-0.216	0.89	-0.322	0.410
	3(C)--1(C)	16	0.294	0.295	-0.732	0.111	-0.405	-0.294	0.92	-0.274	0.376

Table S7: WBI Indices for all nine isomers calculated at B3LYP/6-311+G(d,p) level of theory.

py-1		py-2		ptC-1		ptC-2		ptC-3		spiro-1		spiro-2		spiro-3		spiro-4	
C1-C2	0.70	C1-C2	1.06	C1-C2	1.66	C1-C2	1.56	C1-C2	1.12	C1-C2	1.88	C1-C2	0.96	C1-C2	1.07	C1-C2	0.97
C1-C3	0.70	C1-C3	1.06	C1-C3	0.98	C1-C3	1.14	C1-C3	0.70	C1-C3	0.97	C1-C3	1.01	C1-C3	0.77	C1-C3	1.16
C1-C4	0.70	C2-C3	0.59	C2-C3	0.98	C2-C3	1.14	C2-C3	1.23	C2-C3	0.97	C2-C3	1.01	C2-C3	1.18	C2-C3	1.01
C1-C5	0.70	C3-C4	0.81	C3-C4	0.98	C3-C4	0.86	C3-C4	1.23	C3-C4	0.97	C3-C4	0.97	C3-C4	1.18	C3-C4	0.86
C2-C3	1.10	C3-C5	0.81	C3-C5	0.98	C3-C5	0.86	C3-C5	0.70	C3-C5	0.97	C3-C5	0.97	C3-C5	0.77	C3-C5	0.86
C3-C4	1.10	C4-C5	0.83	C4-C5	1.66	C4-C5	1.03	C4-C5	1.12	C4-C5	1.88	C4-C5	2.44	C4-C5	1.07	C4-C5	1.99
C4-C5	1.10	C4-H8	1.04	C1-H8	0.88	C4-H8	0.91	C1-H8	0.90	C1-H9	0.90	C1-H7	0.90	C1-H8	0.90	C2-H7	0.91
C5-C2	1.10	C4-H9	1.04	C2-H9	0.88	C4-H9	0.91	C1-H9	0.90	C2-H8	0.90	C1-H8	0.90	C1-H9	0.90	C2-H9	0.91
C2-H6	0.91	C5-H6	0.91	C4-H6	0.88	C5-H6	0.91	C5-H6	0.90	C4-H6	0.90	C2-H6	0.90	C5-H6	0.90	C4-H8	0.90
C3-H7	0.91	C5-H7	0.91	C5-H7	0.88	C5-H7	0.91	C5-H7	0.90	C5-H7	0.90	C2-H9	0.90	C5-H7	0.90	C5-H6	0.90
C4-H8	0.91	C1-C2	0.90														
C5-H9	0.91	C1-C3	0.89														

S8

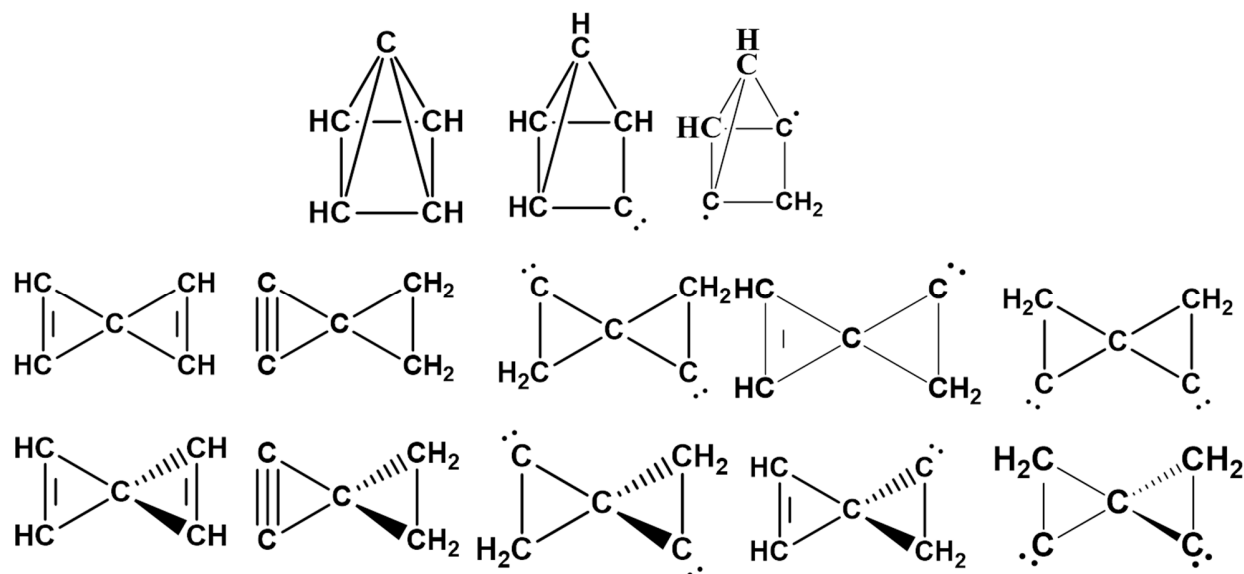Figure S1: Possible 2D structure of initial guess isomers

Figure S2: Optimized geometries of all nine isomers in their triplet spin state calculated at the B3LYP/6-311+G(d,p) level of theory.
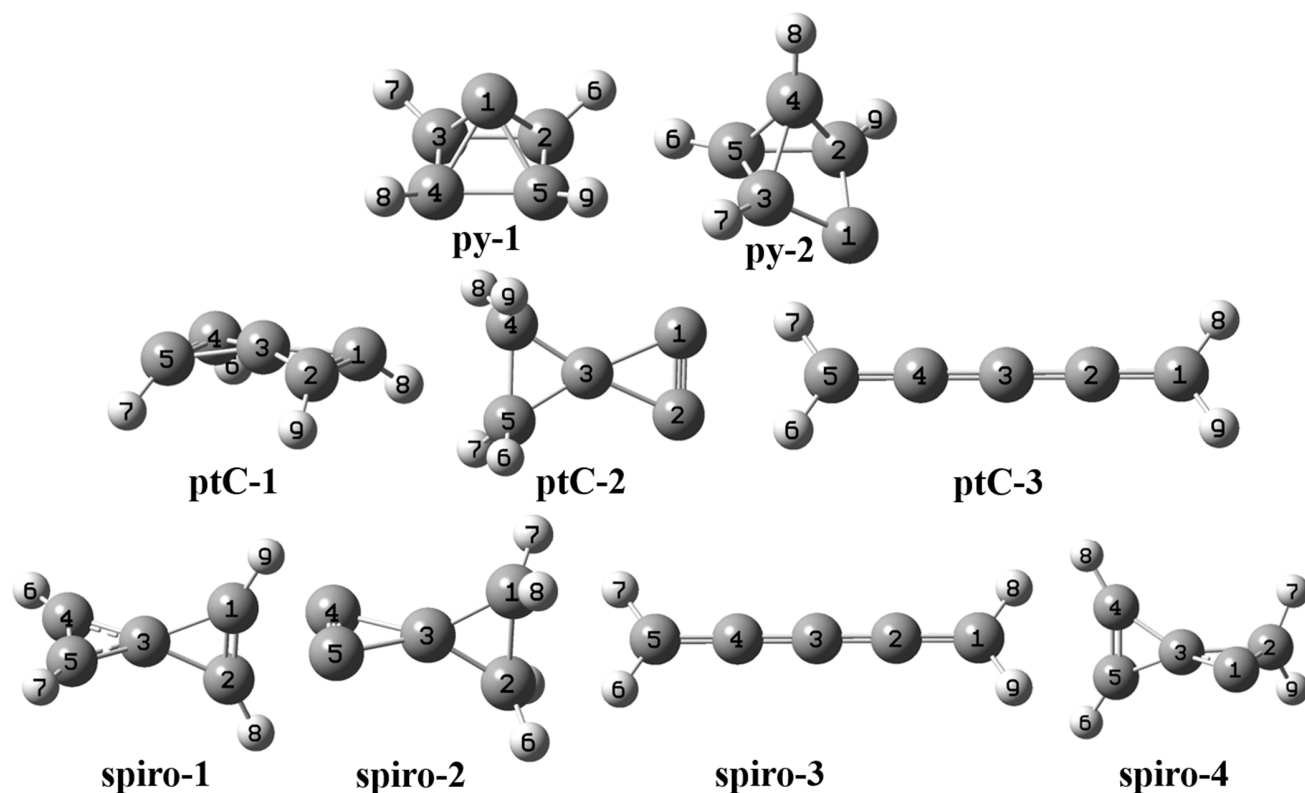
Figure S3: Energy profile and the structural changes of **ptC-1** with respect to the change in spin state with the ground state molecular term symbol and number of imaginary frequencies.
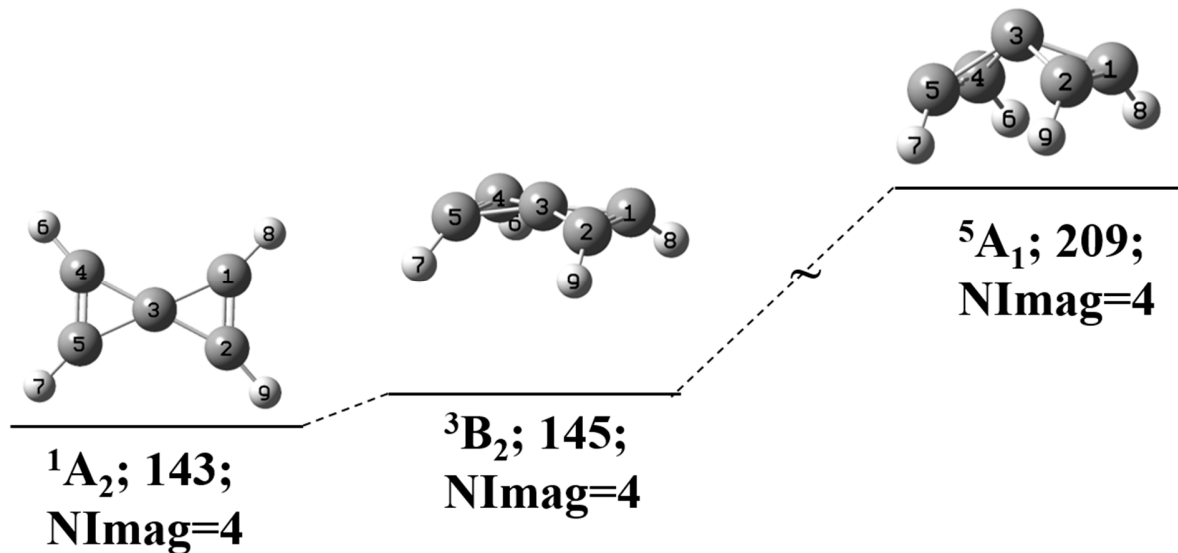

$^1A_2$; 143; NImag=4

$^3B_2$; 145; NImag=4

$^5A_1$; 209; NImag=4

Figure S4: Intrinsic Reaction Coordinate (IRC) for the transition state **ptC-3** calculated at B3LYP/6-311+G(d,p) level of theory.

Backward direction

Forward direction

Figure S5: Energy evolution of isomer **py-1** ($^1A_1$) of C_5H_4 obtained from the AIMD simulation carried out at different temperature (10K, 60K and 120K) and 1 atm pressure for 10000 fs at the B3LYP/6-311+G(d,p) level of theory.
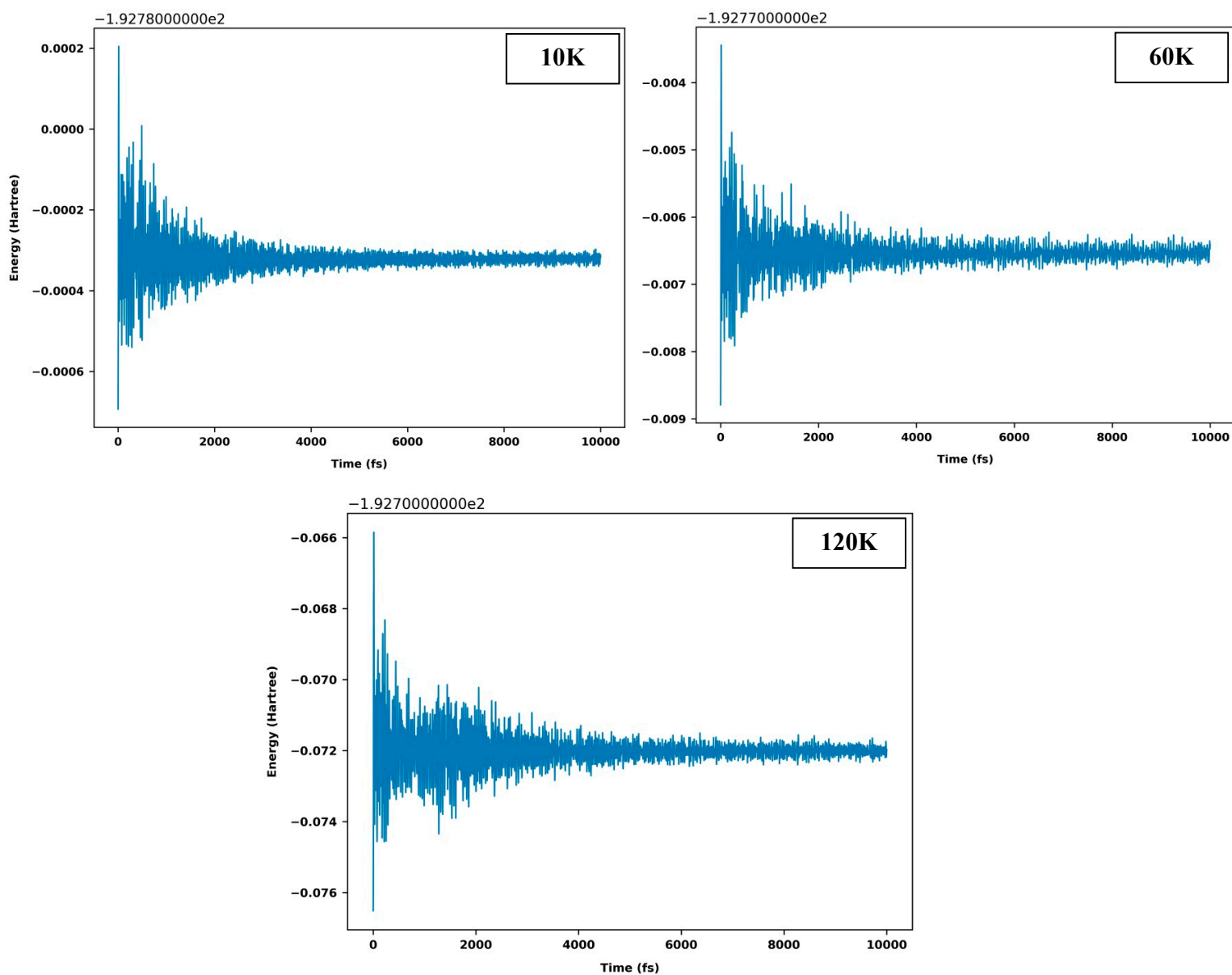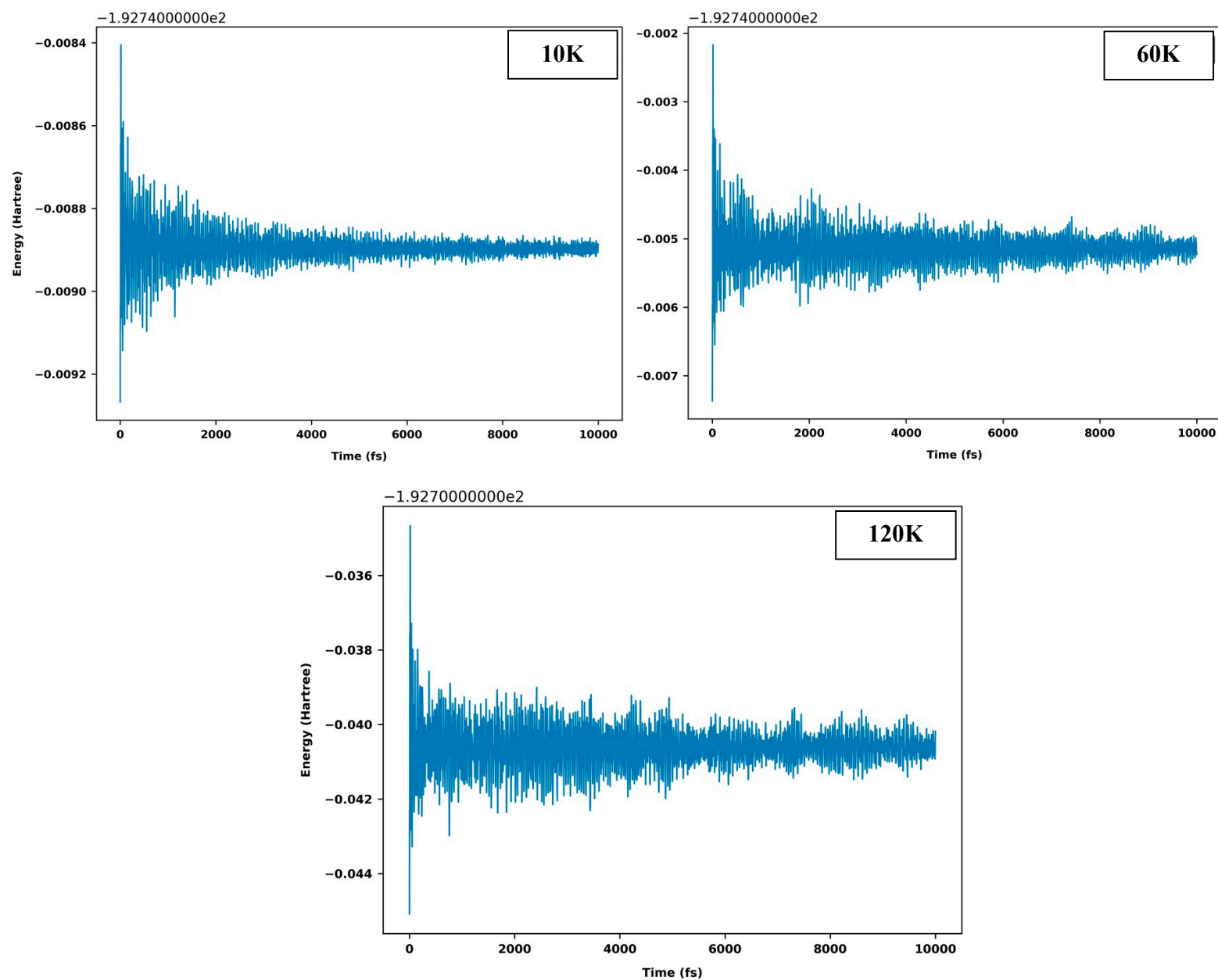
Figure S6: Energy evolution of isomer **py-2** ($^1A'$) of C_5H_4 obtained from the AIMD simulation carried out at different temperature (10K, 60K and 120K) and 1 atm pressure for 10000 fs at the B3LYP/6-311+G(d,p) level of theory.
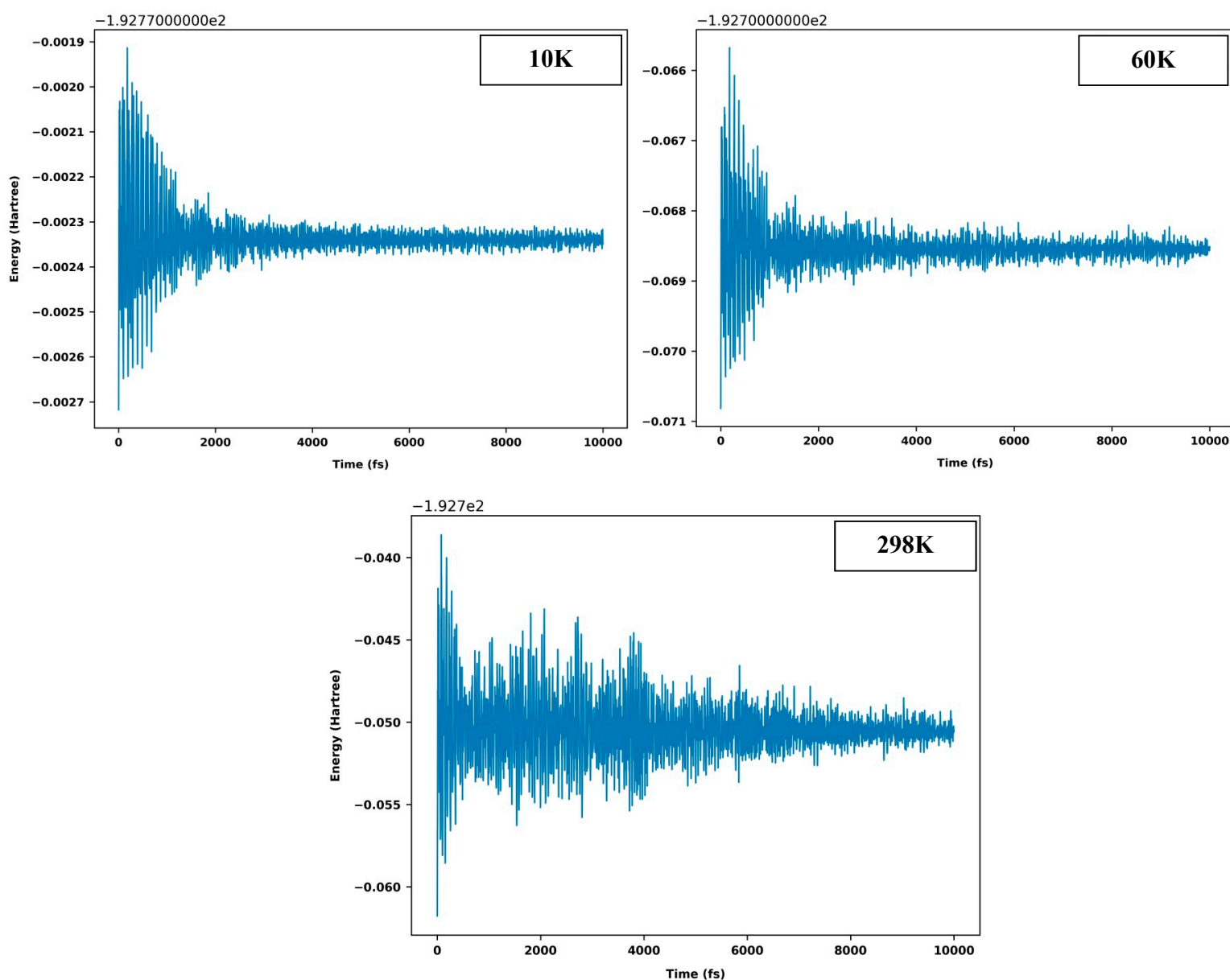
Figure S7: Energy evolution of isomer **spiro-1** (^1E) of C_5H_4 obtained from the AIMD simulation carried out at different temperature (10K, 60K, and 298K) and 1 atm pressure for 10000 fs at the B3LYP/6-311+G(d,p) level of theory.

Figure S8: Energy evolution of isomer **spiro-3** (^{1}B) of C_5H_4 obtained from the AIMD simulation carried out at different temperature (10K, 60K and 120K) and 1 atm pressure for 10000 fs at the B3LYP/6-311+G(d,p) level of theory.
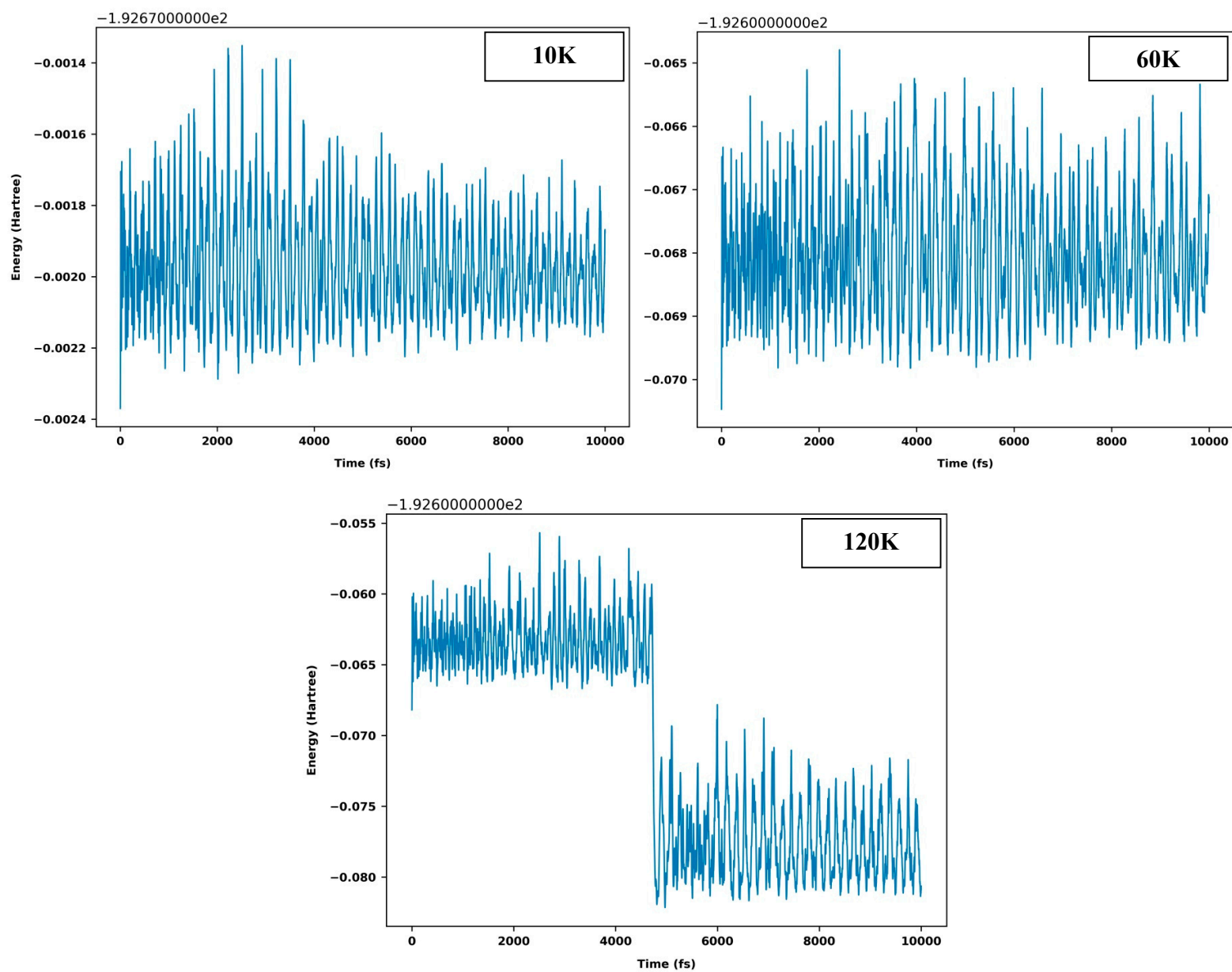
Figure S9: Energy evolution of isomer **spiro-4** ($^1A'$) of C_5H_4 obtained from the AIMD simulation carried out at different temperature (10K, 60K and 120K) and 1 atm pressure for 10000 fs at the B3LYP/6-311+G(d,p) level of theory.