Supporting Information for

Bottom-up Formation of Antiaromatic Cyclobutadiene (*c*-C_4H_4) in Interstellar Ice Analogs

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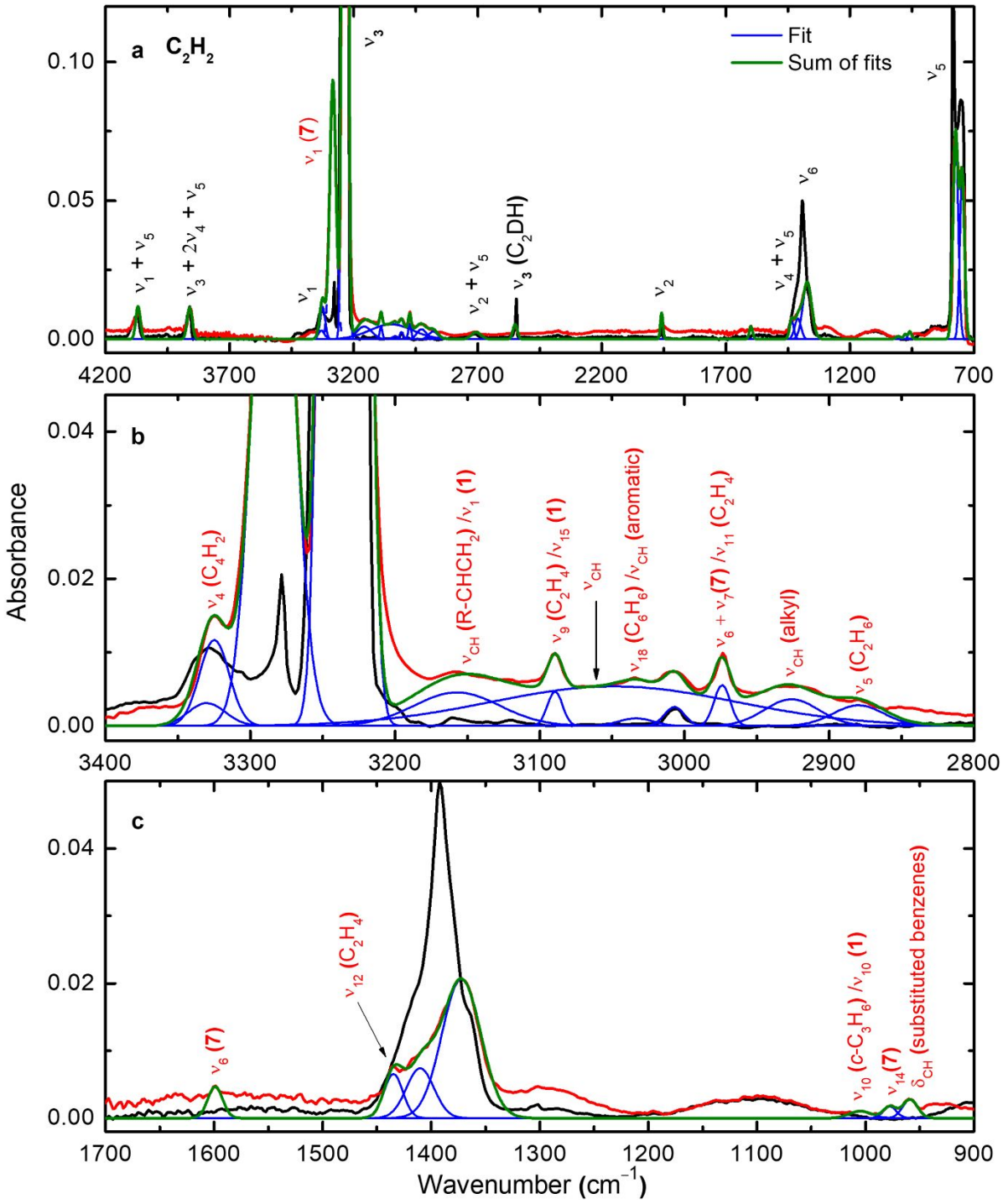


Figure S1. Infrared spectra of an acetylene (C_2H_2) ice before (black) and after (red) electron irradiation at 5 K with magnified view and deconvolution of the region 3400–2800 cm^{-1} (**b**) and region 1700–900 cm^{-1} (**c**). Detailed assignments are compiled in Table S1.

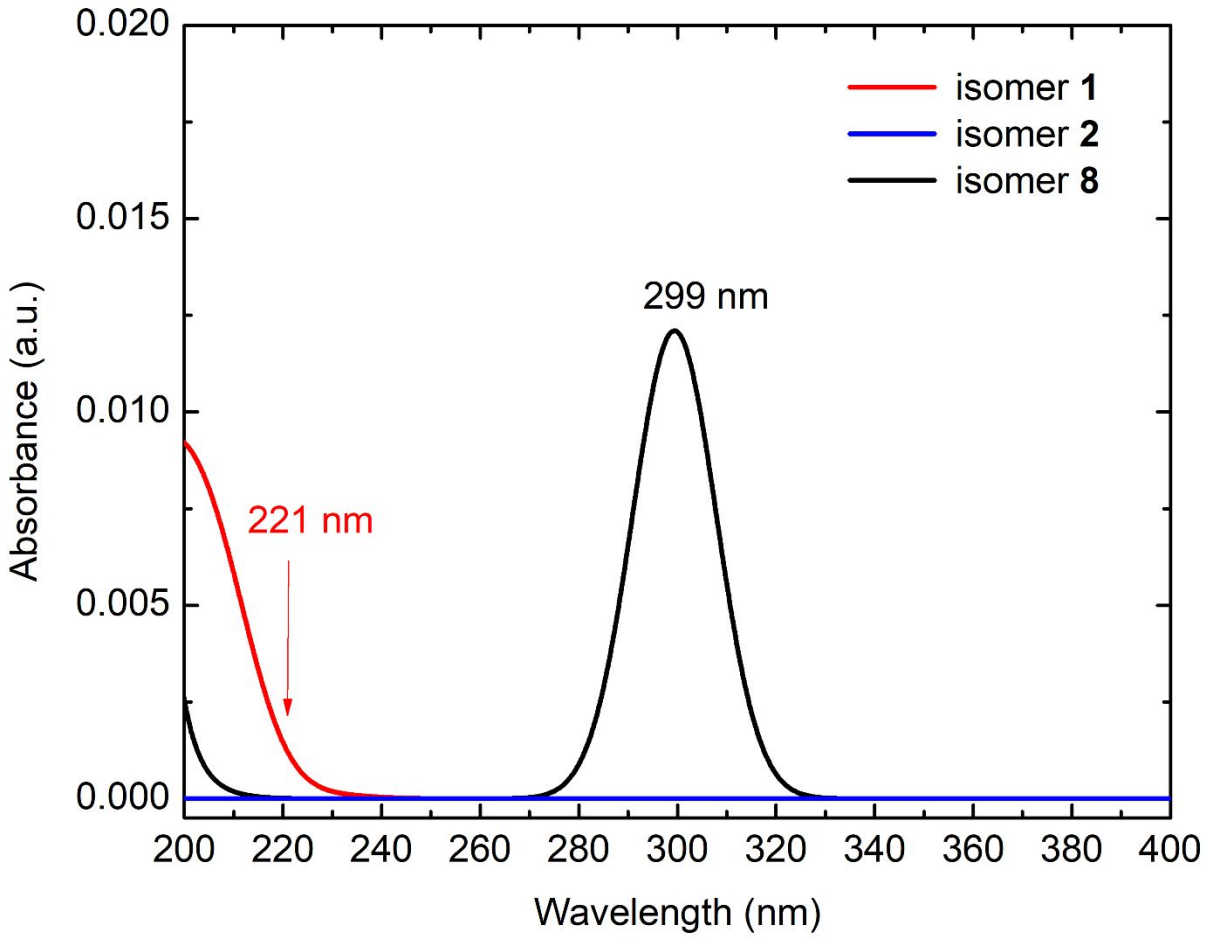


Figure S2. Simulated ultraviolet (UV) spectra of isomers **1**, **2**, and **8** calculated at the TD-B3LYP/cc-pVTZ level of theory. The spectra were convoluted using a Gaussian line shape function with a full width at half maximum (FWHM) of 20 nm.

Table S1. Infrared absorption features observed in acetylene (C_2H_2) ices before and after electron irradiation at 5 K. Assignment labels: stretching (ν) and bending (δ).

Absorption position (cm^{-1})		
Before irradiation	Assignment	References
4067	$\nu_1 + \nu_5$	Ref.[1-3]
3861	$\nu_3 + 2\nu_4 + \nu_5$	Ref.[1,2]
3330	ν_1	Ref.[1,2]
3235	ν_3	Ref.[1,2]
3006	ν_3 ($^{13}C_2H_2$)	Ref.[1-3]
2707	$\nu_2 + \nu_5$	Ref.[1,3]
2549	ν_3 (C_2DH)	Ref.[1]
1959	ν_2	Ref.[1]
1410	$\nu_4 + \nu_5$	Ref.[2]
1393	ν_6	Ref.[1,2]
774, 748	ν_5	Ref.[3,4]
After irradiation	Assignment	References
3325	ν_4 (C_4H_2)	Ref.[1]
3284	ν_1 (**7**)	Ref.[1]
3157[a]	ν_{CH} (R-$CHCH_2$) /ν_1 (**1**)	Ref.[1,5]
3090[a]	ν_9 (C_2H_4) /ν_{15} (**1**)	Ref.[1,5]
3049	ν(CH)	Ref.[6,7]
3033	ν_{18} (C_6H_6)/ν_{CH} (aromatic)	Ref.[1]
2974	ν_6+ν_7 (**7**) /ν_{11} (C_2H_4)	Ref.[1,7]
2926	ν_{CH} (alkyl)	Ref.[4,6]
2880	ν_5 (C_2H_6)	Ref.[1]
1599	ν_6 (**7**)	Ref.[1,7]
1435	ν_{12} (C_2H_4)	Ref.[8,9]
1005[a]	ν_{10} (*c*-C_3H_6) / ν_{10} (**1**)	Ref.[5,9,10]
978	ν_{14} (**7**)	Ref.[7]
959	δ_{CH} (substituted benzenes)	Ref.[3,4]

[a] The absorption band is tentatively assigned to cyclobutadiene (**1**) based on the scaled frequencies calculated at the CCSD(T)=FULL/aug-cc-pVTZ level of theory.[5]

Table S2. Error analysis of adiabatic ionization energies (IEs) and relative energies (ΔE) of distinct C_4H_4 isomers. IEs and ΔE were computed at the CCSD(T)/CBS//B3LYP/cc-pVTZ level of theory including the zero-point vibrational energy corrections. The computed Cartesian coordinates and vibrational frequencies of neutral and ionic species are listed in Table S5. The IE ranges were corrected for thermal and Stark effects by −0.03 eV.[11]

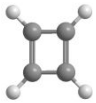
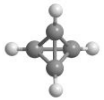
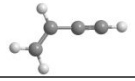
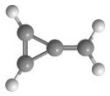
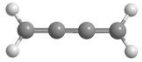
Isomer	Structure	ΔE (kJ mol^{-1})	Experimental IE (eV)	Computed IE (eV)	IE difference to lower bound (eV)	IE difference to upper bound (eV)	IE range after error analysis (eV)
Cyclobutadiene **1**		141		8.00			7.94 – 8.04
Tetrahedrane **2**		249		8.06			8.00 – 8.10
Vinylacetylene **7**		0	9.58 ± 0.02[9]	9.59	−0.03	0.01	9.53 – 9.63
Methylenecyclopropene **8**		98	8.15 ± 0.03[9,12]	8.11	0.01	0.07	8.05 – 8.15
1,2,3-Butatriene **9**		32	9.15 ± 0.02[9,13]	9.14	−0.01	0.03	9.08 – 9.18
Bicyclo[1.1.0]but-3(1)-ene **10**		280		9.12			9.06 – 9.16
					Average −0.01 ± 0.02	Average +0.04 ± 0.03	
					Combined error limits −0.03 – +0.07		

Table S3. Experimental conditions of acetylene (C_2H_2) ices including ice thickness, irradiation parameters, and vacuum ultraviolet (VUV) photon energy.

Exp.	Thickness (nm)	Current (nA)	Irradiation time (s)	Dose (eV/ acetylene)	Photon energy (eV)	Notes
1	830 ± 50	-	-	-	8.20	Blank
2	830 ± 50	109 ± 2	3600 ± 10	9.4 ± 1.5	8.20	
3	830 ± 50	106 ± 2	3600 ± 10	9.1 ± 1.4	8.20	Repeat Exp. 2
4	830 ± 50	107 ± 2	3600 ± 10	9.2 ± 1.4	8.20	Repeat Exp. 2
5	830 ± 50	106 ± 2	3600 ± 10	9.1 ± 1.4	7.80	
6	830 ± 50	107 ± 2	3600 ± 10	9.2 ± 1.4	8.20	299 nm photolysis after irradiation
7	830 ± 50	106 ± 2	3600 ± 10	9.1 ± 1.4	8.20	Repeat Exp. 6
8	850 ± 50	107 ± 2	3600 ± 10	9.2 ± 1.4	8.20	Repeat Exp. 6
9	850 ± 50	111 ± 4	3600 ± 10	9.5 ± 1.5	8.20	221 nm photolysis after irradiation

Table S4. Parameters for the generation of VUV light. The uncertainty for VUV photon energies is less than 0.001 eV.

VUV photon energy (eV)	Nonlinear medium in four-wave mixing	ω_1 laser wavelength (nm)	ω_1 Dye	ω_2 laser wavelength (nm)	ω_2 Dye
8.20 $(2\omega_1 - \omega_2)$	Xenon	249.628	Coumarin 503	715.207	LDS 722
7.80 $(2\omega_1 - \omega_2)$	Xenon	249.628	Coumarin 503	581.119	Pyrromethene 597

Table S5. Cartesian coordinates for selected structures of C_4H_4 isomers. B3LYP/cc-pVTZ optimized Cartesian geometry (distances in Å), electronic energies (in hartree), frequencies (cm^{-1}) intensities (km mol^{-1}), zero-point vibrational energies (ZPVE), extrapolated CCSD(T)/CBS energies (in hartree) and adiabatic ionization energies (IEs) at CCSD(T)/CBS//B3LYP/cc-pVTZ level of theory.

1 radical cation (D_{2h})

C	–0.000000	0.686599	0.750341
C	–0.000000	–0.686599	0.750341
C	0.000000	0.686599	–0.750341
C	0.000000	–0.686599	–0.750341
H	–0.000000	1.453721	1.511268
H	–0.000000	–1.453721	1.511268
H	0.000000	–1.453721	–1.511268
H	0.000000	1.453721	–1.511268

E = –154.4542317
ZPVE = 38.8741 kcal mol^{-1}

Frequency	**Intensity**
276.0704	0.0000
640.4900	84.1796
832.2695	0.9987
841.6395	0.0000
880.8589	0.0000
971.9317	0.0000
991.5550	0.0000
1027.8602	0.0000
1059.1926	1.1356
1211.1668	0.0000
1232.5650	0.0000
1305.0201	71.9589
1491.3494	89.5850
1511.5238	0.0000
3204.7286	0.0000
3226.8412	49.5164
3239.8058	28.6363
3247.9658	0.0000

1 (D_{2h})

C	0.664400	–0.000000	–0.787600
C	–0.664400	–0.000000	–0.787600

C	0.664400	0.000000	0.787600
C	–0.664400	0.000000	0.787600
H	1.427549	–0.000000	–1.550163
H	–1.427549	–0.000000	–1.550163
H	–1.427549	0.000000	1.550163
H	1.427549	0.000000	1.550163

E = –154.7349854
ZPVE = 38.2835 kcal mol^{-1}

Frequency	**Intensity**
540.8596	0.0000
587.3077	127.2477
604.2518	0.0000
698.4518	9.4786
852.3092	0.0000
889.3490	0.0000
890.7646	0.0000
952.1803	0.0000
1060.4766	0.0901
1111.8341	0.0000
1192.7936	0.0000
1265.2261	39.0248
1626.9288	0.0000
1633.6769	4.5552
3193.5687	0.0000
3209.0823	12.8147
3230.1635	20.7511
3240.4735	0.0000

2 radical cation (C_1)

C	–0.592346	–0.607635	0.382981
C	–0.607678	0.592308	–0.382984
C	0.607676	–0.592305	–0.382987
C	0.592342	0.607630	0.382992
H	–1.174862	1.144947	–1.113087
H	1.145233	1.174579	1.113087
H	1.174901	–1.144918	–1.113078
H	–1.145244	–1.174591	1.113066

E = –154.4046128
ZPVE = 36.9385 kcal mol^{-1}

Frequency	**Intensity**
485.9159	0.0000
612.6863	13.2732

648.9106	48.8967
709.1626	0.0000
759.4133	0.0000
764.8516	46.0211
764.8893	46.0190
930.4649	0.0000
999.4507	24.9013
999.4625	24.8847
1045.2343	0.0000
1306.5094	3.0925
1306.6953	3.0815
1445.3571	0.0000
3255.0240	100.4067
3258.3457	112.9764
3258.3500	112.9214
3288.0964	0.0000

2 (T_d)

C	0.521179	0.521179	0.521179
C	–0.521179	–0.521179	0.521179
C	0.521179	–0.521179	–0.521179
C	–0.521179	0.521179	–0.521179
H	–1.137600	–1.137600	1.137600
H	–1.137600	1.137600	–1.137600
H	1.137600	–1.137600	–1.137600
H	1.137600	1.137600	1.137600

E = –154.6957648
ZPVE = 37.3359 kcal mol^{-1}

Frequency	Intensity
574.7036	0.0000
574.7036	0.0000
774.7601	65.6948
774.7601	65.6948
774.7601	65.6948
843.6015	0.0000
843.6016	0.0000
891.6832	0.0000
891.6832	0.0000
891.6833	0.0000
1149.5326	2.9279
1149.5326	2.9279
1149.5326	2.9279
1458.2091	0.0000

3334.1033	11.8500
3334.1033	11.8500
3334.1033	11.8500
3371.7694	0.0000

7 radical cation (C_s)

C	0.621817	–0.528679	0.000000
C	–0.138053	–1.687735	0.000000
H	0.343051	–2.657611	0.000000
H	–1.219991	–1.648712	0.000000
C	0.036481	0.714859	–0.000000
H	1.706165	–0.584653	0.000000
C	–0.463499	1.832286	–0.000000
H	–0.902586	2.808515	–0.000000

E = –154.4588263
ZPVE = 37.6867 kcal mol^{-1}

Frequency	**Intensity**
211.0198	5.5624
278.5302	13.1006
519.5787	1.7658
551.5130	9.3273
680.0409	48.3325
773.3045	13.8438
891.7525	27.4534
937.1157	0.9330
1066.2661	9.1755
1133.1350	0.5054
1278.6399	30.4247
1437.5286	65.2393
1538.2685	38.7268
2123.8653	122.3631
3146.2361	16.1624
3156.3567	15.0496
3256.4676	15.3200
3382.5859	138.8371

7 (C_s)

C	–0.674648	–0.467653	0.000000
C	–1.690583	0.396652	0.000000
H	–2.713562	0.048104	0.000000
H	–1.525819	1.465184	0.000000
C	0.697193	–0.099614	–0.000000
H	–0.878465	–1.533400	0.000000

C	1.867876	0.174579	–0.000000
H	2.898441	0.426808	–0.000000

E = –154.7979450
ZPVE = 38.2649 kcal mol^{-1}

Frequency	**Intensity**
225.9582	2.6766
320.5892	8.8670
559.7306	4.9591
649.3593	47.2681
675.8635	44.5507
706.9073	1.7781
893.0959	2.2555
962.5901	42.3668
1012.8555	14.7567
1114.7889	3.7489
1325.6964	0.4594
1449.4179	3.0436
1669.2591	9.4554
2204.9388	0.4066
3137.4281	4.9392
3149.7069	3.3775
3237.4324	6.1240
3471.0886	70.8762

8 radical cation (C_{2v})

C	0.000000	0.674371	–1.010628
C	–0.000000	–0.674371	–1.010628
C	–0.000000	–0.000000	0.194911
H	0.000000	1.600278	–1.564602
H	–0.000000	–1.600278	–1.564602
C	–0.000000	–0.000000	1.597774
H	–0.000000	0.935016	2.139718
H	–0.000000	–0.935016	2.139718

E = –154.4690262
ZPVE = 37.8093 kcal mol^{-1}

Frequency	**Intensity**
235.7671	0.0000
360.2077	4.5638
419.2655	20.0369
817.4191	5.9055
837.0901	0.1387
880.0582	58.6573

953.4758	2.1478
991.1747	0.0000
1000.8620	28.5731
1082.0881	8.4150
1268.8218	24.6507
1441.1377	47.5163
1477.9502	31.1013
1743.9048	18.6326
3154.9643	18.1242
3239.0267	75.6043
3270.9076	10.4368
3273.8833	39.0069

8 (C_{2v})

C	0.000000	0.656758	–1.002837
C	–0.000000	–0.656758	–1.002837
C	–0.000000	–0.000000	0.275660
H	0.000000	1.567085	–1.576184
H	–0.000000	–1.567085	–1.576184
C	–0.000000	–0.000000	1.600737
H	–0.000000	0.926314	2.156709
H	–0.000000	–0.926314	2.156709

E = –154.7616607
ZPVE = 37.9782 kcal mol^{-1}

Frequency	Intensity
360.8519	3.3816
430.8942	24.5831
686.6364	35.2667
715.9854	0.0000
775.6980	70.6166
841.9014	0.4481
849.6912	6.1322
913.8828	0.0000
1023.4632	8.0831
1069.2797	8.2380
1124.7067	10.5199
1460.7691	1.6649
1603.8735	25.3360
1824.9957	206.1271
3144.8718	3.6077
3226.2421	11.5584
3235.5897	0.7843
3276.7831	1.8580

9 radical cation (D_2)

C	0.000000	0.000000	–0.629535
C	0.000000	–0.000000	–1.953708
H	0.318309	0.876968	–2.512401
H	–0.318309	–0.876968	–2.512401
C	–0.000000	0.000000	0.629535
C	–0.000000	0.000000	1.953708
H	0.318309	–0.876968	2.512401
H	–0.318309	0.876968	2.512401

E = –154.4657874
ZPVE = 36.5689 kcal mol^{-1}

Frequency	**Intensity**
205.4230	14.1285
211.8713	14.4922
370.9531	0.2673
497.7136	0.3058
695.7925	0.0000
881.3679	0.0000
953.8952	0.9512
954.8397	31.9212
991.5916	26.4948
1000.8181	3.6934
1370.3175	70.7033
1425.3344	0.0000
1561.4705	2.2031
1897.1491	0.0000
3093.9898	0.0000
3095.7078	164.0098
3186.0397	75.6746
3186.0506	9.4056

9 (D_2)

C	0.000000	0.631692	–0.000000
C	0.000000	1.943248	–0.000000
H	–0.924750	2.507776	0.000231
H	0.924750	2.507776	–0.000231
C	–0.000000	–0.631692	–0.000000
C	–0.000000	–1.943248	–0.000000
H	0.924750	–2.507776	0.000231
H	–0.924750	–2.507776	–0.000231

E = –154.7925173

ZPVE = 37.6236 kcal mol^{-1}

Frequency	**Intensity**
225.1199	6.9536
230.6334	6.0168
362.2186	0.0000
574.8887	0.0000
778.2503	0.0000
891.4062	0.0000
895.3525	95.1505
904.5415	0.0000
1026.1528	0.0000
1045.5381	0.7686
1412.5879	0.0359
1471.2333	0.0000
1681.6450	21.5846
2199.1118	0.0000
3116.5403	0.0000
3119.4130	6.1441
3191.5661	4.6841
3191.8699	0.0000

10 radical cation (C_2)

C	0.676053	0.375244	0.151142
C	–0.596733	1.075098	0.151266
C	–0.676053	–0.375244	0.151142
H	–0.898590	1.618931	–0.755586
H	–0.898591	1.618932	1.058096
C	0.596733	–1.075098	0.151266
H	0.898591	–1.618932	1.058096
H	0.898590	–1.618931	–0.755586

E = –154.3540120
ZPVE = 36.4443 kcal mol^{-1}

Frequency	**Intensity**
251.2275	17.0642
545.3570	98.0578
840.3421	0.0000
847.8097	0.0000
868.2537	0.0000
886.2857	0.0000
944.6038	0.0000
954.9375	3.9879
1074.9159	44.0676
1120.4299	0.0000

1143.4530	0.0000
1328.7677	37.8635
1398.2172	0.0000
1417.9691	55.3693
2931.9543	137.4841
2963.0963	0.0008
2983.2028	0.0003
2992.3519	103.2850

10 (C_2)

C	0.000006	0.681976	–0.376604
C	–1.228680	0.000001	0.115464
C	–0.000006	–0.681976	–0.376604
H	–2.054448	0.000006	–0.581041
H	–1.524452	–0.000011	1.166788
C	1.228680	–0.000001	0.115464
H	1.524452	0.000011	1.166788
H	2.054448	–0.000007	–0.581041

E = –154.6831688
ZPVE = 38.8382 kcal mol^{-1}

Frequency	**Intensity**
367.2913	3.7531
406.2638	138.5603
717.1912	0.0000
931.6230	15.3382
934.6460	1.7423
1068.0418	0.9411
1072.3402	15.0439
1108.2552	0.0000
1134.7274	1.3147
1163.3747	0.0000
1336.9641	31.2257
1411.2847	1.7210
1515.2500	5.0124
1557.6431	2.0370
3031.3870	69.2944
3032.3357	67.3020
3188.3766	3.8315
3190.7425	3.8634

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