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Supporting Information

Gas-Phase Synthesis of the Elusive Cyclooctatetraenyl Radical (C_8H_7) via Triplet Aromatic Cyclooctatetraene (C_8H_8) and Non-Aromatic Cyclooctatriene (C_8H_8) Intermediates

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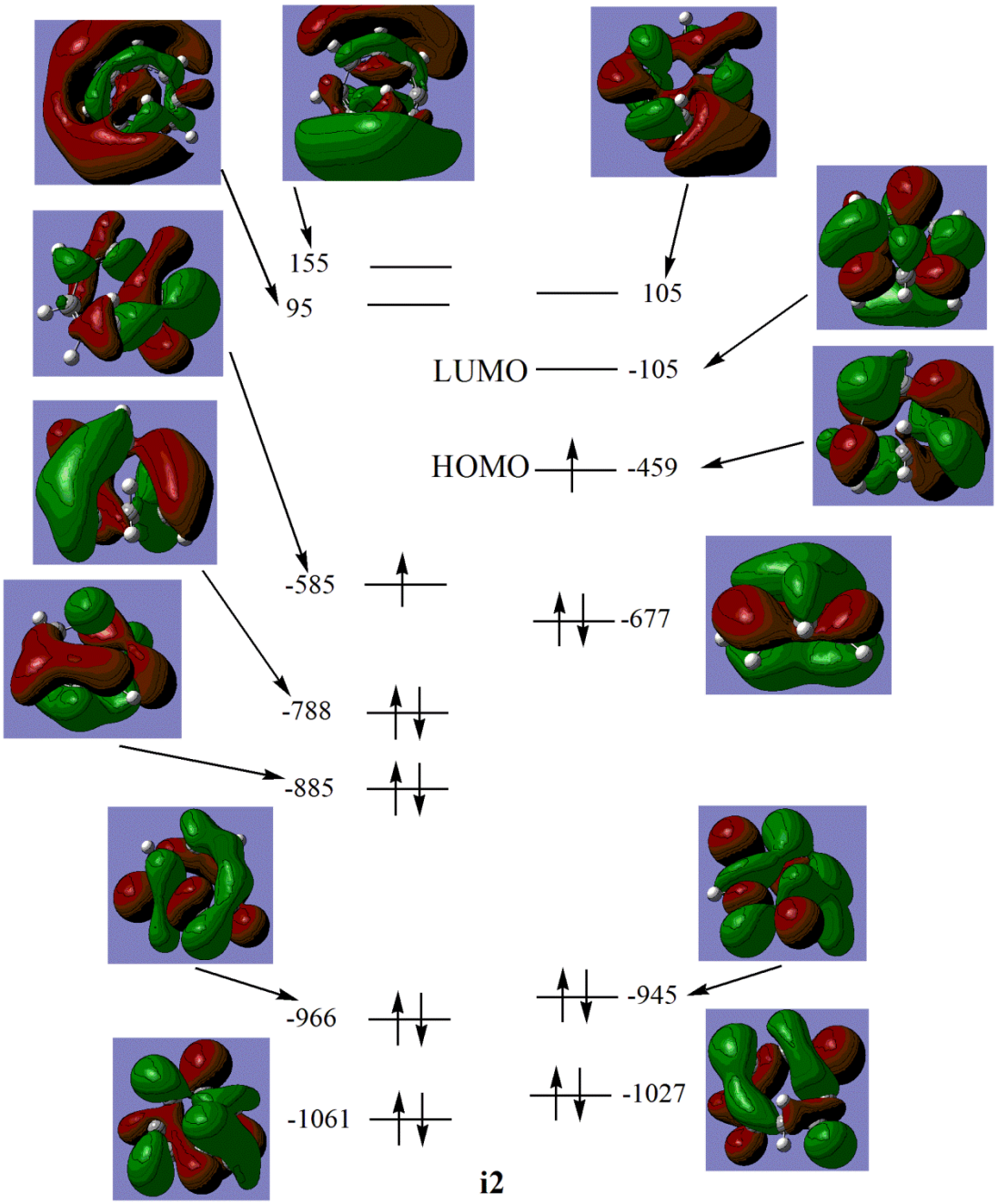
Experimental Procedures

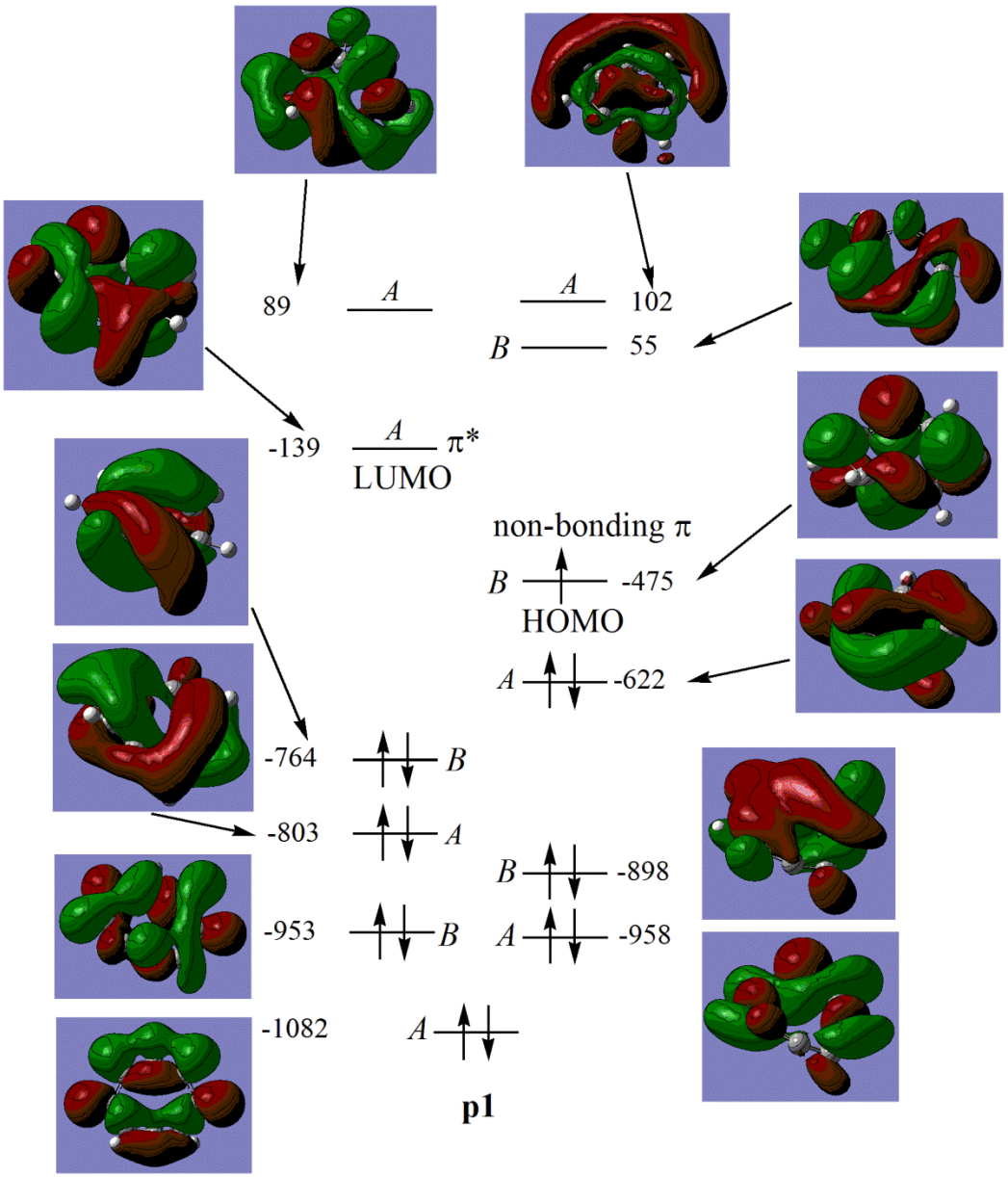
Experimental: The elementary gas phase reaction of atomic carbon ($C(^3P_j)$) with 1,3,5-cycloheptatriene (C_7H_8; TCI America; > 95 %) was studied under single collision conditions in a crossed molecular beams machine.[1-4] A pulsed molecular beam of helium-seeded ground state carbon atoms was produced in the primary source chamber by ablating a rotating graphite rod with a 266 nm output of a Nd:YAG laser (Quanta Ray Pro 270, Spectra Physics) operating at 30 Hz and 10-13 mJ per pulse. The ablated species were seeded in helium carrier gas (Airgas; 99.9999 %) with a backing pressure of 3040 Torr released from a piezoelectric pulsed valve operating at a repetition rate of 60 Hz, a pulse width of 80 µs, and a peak voltage of -400 V. The pulsed carbon molecular beam passed through a skimmer and was velocity selected by a four-slot chopper wheel rotating at 120 Hz. The on-axis characterization of the pulsed carbon beam at *m*/*z* 12 (C^+) indicated a peak velocity (v_p) of 2537 ± 122 ms^{-1} and a speed ratio (S) of 3.6 ± 0.5. The carbon beam was crossed perpendicularly by a pulsed, supersonic cycloheptatriene (C_7H_8) beam seeded in argon (Airgas; 99.9999 %) generated by a second piezoelectric pulsed valve at a backing pressure of 550 Torr with a repetition rate of 60 Hz, a pulse width of 80 µs, and a peak voltage of -400 V in the secondary source chamber. The cycloheptatriene molecular beam was characterized through v_p and S to be 588 ± 20 ms^{-1} and 13.7 ± 0.4, respectively, yielding a collision energy of 32 ± 4 kJ mol^{-1}. The reactively scattered products were detected with a rotatable, triply differentially pumped, quadrupole mass spectrometer (QMS) operated in the time-of-flight (TOF) mode. The neutral products were ionized with an electron impact ionizer at an electron energy of 40 eV and an emission current of 1.4 mA. The mass-selected ions were accelerated towards an aluminum coated stainless steel target held at -22.5 kV; an electron cascade was initiated, when an ion hit the aluminum coated target, and was accelerated toward an aluminum coated organic scintillator generating a photon pulse to be detected by a photomultiplier tube (PMT; Burle Model 8850; -1.35 kV). The signal from the PMT was then filtered by a discriminator (Advanced Research Instruments, Model F-100TD) at a level of 1.6 mV prior to directing into a Stanford Research System SR430 Multi-Channel Scaler to record the TOF spectra. The detector is rotatable within the plane as defined by the carbon and cycloheptatriene beams. Up to 2×10^6 TOF spectra were recorded at each angle. The laboratory angular distribution was acquired by integration of the TOF spectra at each collection angle and normalizing for the accumulation time and fluctuations in the carbon beam intensity. To gain additional information on the chemical dynamics and underlying reaction mechanism, TOF spectra and the laboratory angular distribution were transformed from the laboratory frame into the center-of-mass reference frame using a forward-convolution routine.[5,6] This approach initially presumes an angular flux distribution $T(\theta)$ and translational energy flux distribution $P(E_T)$ in the center-of-mass system assuming mutual independence. The laboratory data (TOF spectra and laboratory angular distribution) are then calculated from the $T(\theta)$ and $P(E_T)$ and convoluted over the apparatus functions to obtain a simulation of the experimental data. The crucial output of this fitting routine is the product flux contour map, $I(\theta,u) = P(u) \times T(\theta)$, which reports the intensity of the reactively scattered products (I) as a function of the center-of-mass scattering angle (θ) and product velocity (u). This plot is called the reactive differential cross section and can be seen as the image of the chemical reaction.

Theoretical: Geometries of the 1,3,5-cycloheptatriene reactant, C_8H_7 radical products, and various triplet intermediates and transition states on the C_8H_8 PES were optimized at the hybrid density functional B3LYP level of theory[7,8] with the 6-311G** basis set. The same B3LYP/6-311G** method was used to calculate vibrational frequencies, which were utilized to compute zero-point energy (ZPE) corrections, to identify the stationary structures as local minima or first-order saddle points, and to compute rate constants for unimolecular reaction steps. To evaluate more accurate relative energies, single-point energies at the optimized geometries were recalculated using the G3(MP2,CC)//B3LYP approach[9,10], which provides accuracy for relative energies within 10 kJ mol^{-1}. The electronic structure calculations were carried out using the GAUSSIAN 09[11] and MOLPRO 2010[12] program packages. Relative yields for various H loss channels from C_8H_8 under single-collision conditions were computed using Rice−Ramsperger−Kassel−Marcus (RRKM) theory[13-15]. The rate constants were calculated as functions of available internal energy, where the internal energy was taken as a sum of the energy of chemical activation in the $C(^3P)$ + 1,3,5-cycloheptatriene reaction and the collision energy, assuming that it predominantly converts into internal vibrational energy. Since the RRKM calculations were performed for single-collision conditions at zero-pressure limit, only a single total-energy level was considered throughout.[16] The harmonic approximation was employed to compute numbers and densities of states. Using the calculated rate constants, branching ratios of various channels were computed by solving first-order kinetic equations within the steady-state approximation for unimolecular isomerization and fragmentation steps of the initial reaction intermediates **i1** and **i3**.



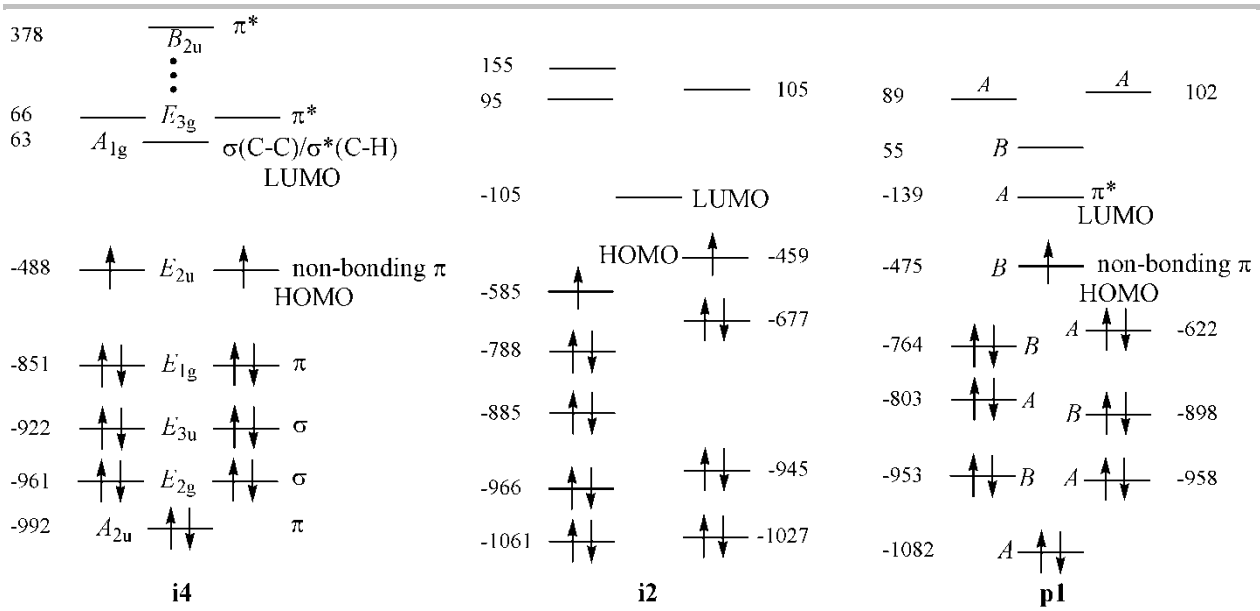
(a)

Figure S1. Molecular orbital diagrams (a) for the decomposing intermediate **i2 (**2,4,7-cyclooctatriene, C_1) on the triplet surface, (b) for the 1,2,4,7-cyclooctatetraenyl radical (C_8H_7, C_2) product **p1**, and (c) comparison of molecular orbital energy levels of **i4**, **i2**, and **p1**. The energy levels are shown in kJ mol^{-1}.



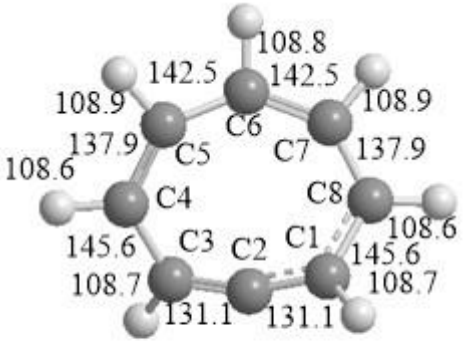
(b)

Figure S1. (Continued)

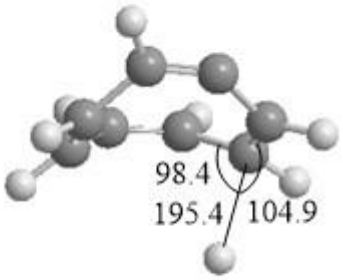


(c)

Figure S1. (Continued-2)



p1



ts **i2-p1**

Figure S2. Bond lengths in the main product **p1** and bond lengths and bond angles in the atomic hydrogen loss transition state **i2**-**p1** are given in pm and degrees, respectively.

Discussion about the singlet surface

Addressing a possible role of the singlet surface, we note that in the previous studies of reactions of ground state atomic carbon with unsaturated hydrocarbons, a spin-flip via intersystem crossing (ISC) was found to play an important role only for the carbon plus acetylene reaction, in which the system crosses over to the singlet C_3H_2 surface and can form the $C_3(X^1\Sigma_g+)$ + H_2 products.[17] This unique behavior was attributed to a relative long lifetime of the decomposing C_3H_2 complexes caused by the fact that the products on the triplet surface, *c*- and *l*-C_3H are nearly thermoneutral or slightly exoergic. Only their relatively long lifetime allows the triplet-singlet ISC to occur. Another reaction of ground state carbon atoms, in which ISC might play a role is carbon plus benzene, but only in bulk conditions, not in gas phase molecular beam experiments.[17] In the reactions involving larger alkynes and alkenes, much more exoergic products can be formed and the lifetime of the triplet intermediates is shorter and hence no evidence of ISC was observed so far. The present reaction is highly exoergic as well, and our statistical (RRKM) calculations indicate that the lifetimes of the triplet intermediates are short, in the range of 25-75 ns at the experimental collision energy. The predominant role of the triplet surface is evidenced by the existence of an exit barrier for the hydrogen atom loss, based on the shape of the translational energy distribution; the hydrogen atom loss from any singlet intermediate is barrierless. Although the role of the singlet surface cannot be completely ruled out, it is unlikely. First, according to our calculations of the singlet surface, the singlet-triplet energy gaps for all critical triplet intermediates involved are large, 161, 135, and 127 kJ mol^{-1} for **i2**, **i3**, and **i4**, respectively, with singlet states lying lower in energy (Supporting Information). The energy gaps that high make ISC a less likely process; for comparison, in C_3H_2 ISC was found to be efficient between triplet and singlet structures separated only by 50 kJ mol^{-1} with triplet being more favorable and still only at low collision energies.[18] Second, if singlet isomers are formed via ISC, their calculated lifetimes with respect to hydrogen atom elimination are up to three orders of magnitude longer (2-60 μs). Therefore, the C_8H_8 singlet isomers, if produced, could have survived in the reaction chamber and then be ionized and detected. This however is not the case in the present experiment.

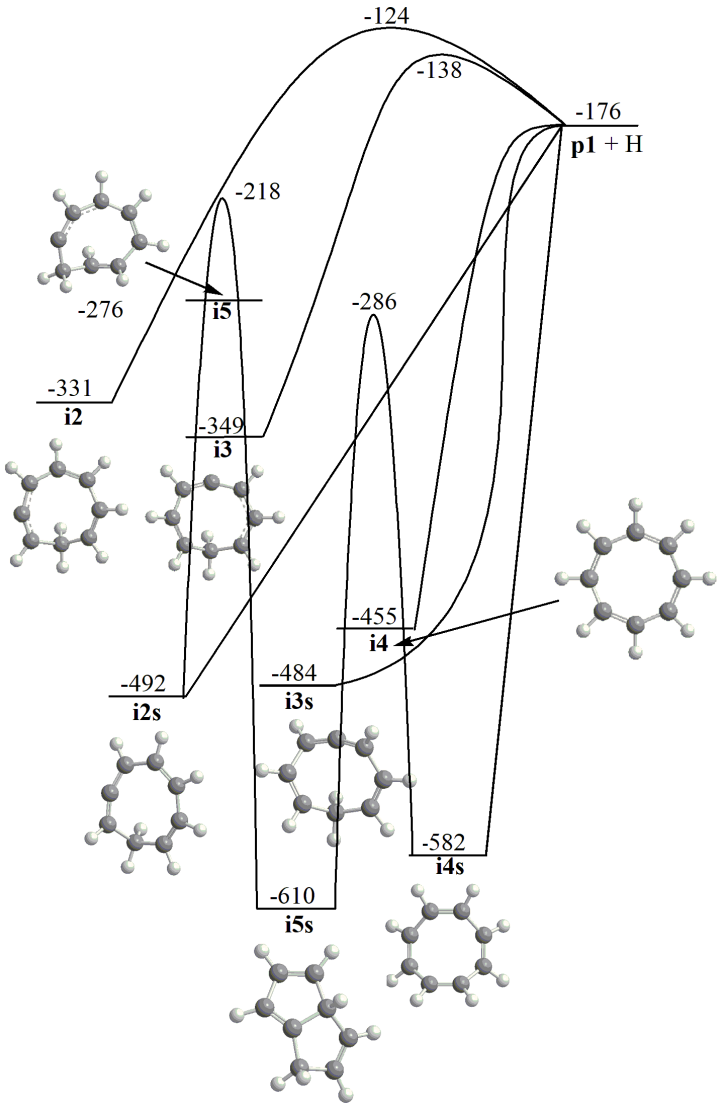
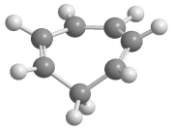
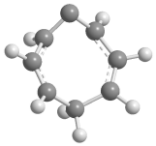
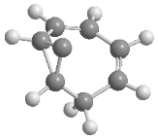
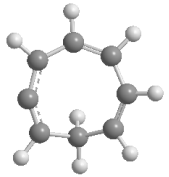
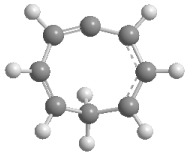
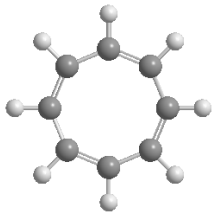
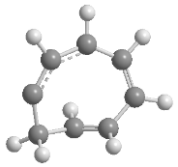
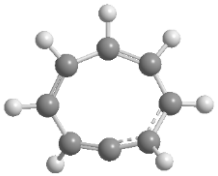
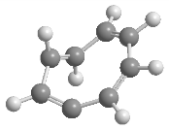


Figure S3. Fragment of the singlet C_8H_8 PES that can be accessed by triplet-singlet intersystem crossing in the vicinity of triplet intermediates **i2**-**i5**. All relative energies are shown in kJ mol^{-1} with respect to the $C(^3P)$ + C_7H_8 reactants.

Table S1. Optimized Cartesian coordinates (in Å) and vibrational frequencies (in cm^{-1}) for all stationary structures.

Structure	Coordinates			Frequencies		
1,3,5-cycloheptatriene 	6 0 0.255703	-1.417716	0.680838	214.2007	295.2611	356.2407
	6 0 0.255703	-1.417716	-0.680838	417.5620	431.8578	610.4532
	6 0 -0.248870	-0.360149	-1.527547	667.8938	725.3930	760.9588
	6 0 -0.248870	-0.360149	1.527547	813.2356	890.4976	921.1552
	6 0 -0.248870	0.951946	-1.221424	938.8788	960.4329	977.9240
	6 0 -0.248870	0.951946	1.221424	983.2979	1001.3070	1040.0880
	6 0 0.456430	1.484915	0.000000	1067.8427	1210.3505	1221.4227
	1 0 0.538483	-2.342005	1.177961	1247.3754	1269.2488	1327.5448
	1 0 0.538483	-2.342005	-1.177961	1385.7664	1424.3800	1475.5665
	1 0 -0.680782	-0.669571	-2.476233	1480.6603	1572.7814	1663.2648
	1 0 -0.680782	-0.669571	2.476233	1670.9291	2992.9632	3088.3701
	1 0 -0.757659	1.654307	-1.875029	3124.8049	3130.6974	3137.5103
	1 0 -0.757659	1.654307	1.875029	3152.1701	3158.4702	3163.1804
	1 0 1.499013	1.140161	0.000000			
	1 0 0.466769	2.575908	0.000000			
i0 (ts **i3**-**i3**) 	6 0 -1.753400	0.083737	-0.136878	514.4247*i*	74.0510	158.2441
	6 0 -0.424030	-1.456777	-0.385587	237.3086	350.3716	399.7129
	6 0 0.954245	-1.472230	0.156966	447.3517	493.9021	634.2829
	6 0 -1.092721	1.347282	0.159625	673.2567	701.9547	733.6203
	6 0 1.746492	-0.405500	0.228472	779.6552	816.0227	871.0929
	6 0 0.205352	1.703428	0.170440	919.4117	952.7248	966.3657
	6 0 1.395357	0.939049	-0.375517	969.3894	1006.7080	1037.1564
	1 0 -2.664982	0.172481	-0.739634	1106.3208	1188.6641	1204.2177
	1 0 -0.596465	-1.752569	-1.423320	1241.1901	1258.1401	1284.6884
	1 0 1.268387	-2.418847	0.595822	1358.5495	1374.2058	1386.4509
	1 0 -1.806697	2.138279	0.396771	1421.6130	1475.3600	1641.4935
	1 0 2.714894	-0.501247	0.711424	1698.2803	2977.3152	3015.0408
	1 0 0.419549	2.720762	0.485416	3055.8910	3077.2313	3084.4204
	1 0 2.270186	1.589564	-0.318553	3109.3349	3145.7305	3151.2710
	1 0 1.209619	0.777112	-1.447742			
	6 0 -1.500379	-1.193244	0.472447			
i1 	6 0 -1.435168	-0.628942	-0.118694	157.4186	231.5945	277.5564
	6 0 -1.190451	1.016776	0.058444	349.2926	402.3314	462.0406
	6 0 0.088109	1.609399	-0.331692	533.8174	609.6206	663.9902
	6 0 1.335493	1.111556	-0.155109	716.7522	809.5799	825.8966
	6 0 0.999542	-1.335525	0.178482	862.5362	874.8608	910.0382
	6 0 1.697332	-0.200409	0.353567	956.2503	972.1817	991.6852
	1 0 -2.384628	-0.847008	-0.619055	1000.1256	1012.7027	1023.4316
	1 0 -2.056177	1.598290	-0.264047	1094.5326	1207.6960	1222.4359
	1 0 0.009700	2.601474	-0.768474	1247.1607	1258.7794	1301.0822
	1 0 2.166080	1.769560	-0.398851	1346.5958	1396.7529	1424.2942
	1 0 1.385719	-2.249644	0.617997	1461.6995	1472.5682	1604.0922
	1 0 2.645522	-0.260905	0.882499	1675.3845	2981.8560	3024.3013
	6 0 -1.421674	0.050763	1.135944	3053.3692	3060.4089	3125.0512

	6 0 -0.260412 -1.451129 -0.636965 1 0 -0.062448 -1.149650 -1.676065 1 0 -0.580402 -2.497049 -0.677875	3135.0315 3151.5041 3163.6207	
i2 	6 0 1.423854 1.212052 -0.111850 6 0 -1.147211 1.448244 -0.134073 6 0 -1.782065 0.241101 0.246152 6 0 -1.389299 -1.082514 0.160115 6 0 1.109857 -1.308602 -0.228306 6 0 -0.176693 -1.697124 -0.330354 1 0 2.305019 1.806146 -0.340546 1 0 -1.817358 2.296407 -0.261785 1 0 -2.819121 0.375797 0.547437 1 0 -2.182058 -1.795174 0.374937 1 0 1.858277 -1.919747 -0.724125 1 0 -0.346477 -2.650501 -0.829517 6 0 0.203031 1.701182 -0.348492 6 0 1.626293 -0.135821 0.567304 1 0 1.106338 -0.107607 1.532781 1 0 2.688768 -0.276429 0.777833	137.5265 156.8637 258.0908 295.5786 379.1963 441.0245 553.2308 557.9836 667.3936 690.6487 722.6419 758.6546 796.2785 845.4846 859.0452 904.6278 923.7071 977.6189 980.7823 1018.2075 1060.6105 1150.4159 1214.7068 1257.9004 1280.9159 1292.1542 1319.5056 1352.8319 1423.6110 1458.8851 1482.7397 1501.2202 1584.3548 1645.6758 3010.2674 3076.2058 3103.5017 3108.3710 3122.2364 3129.7370 3141.1615 3154.1495	
i3 	6 0 1.314604 -1.303702 0.064058 6 0 -1.314746 -1.303502 0.064553 6 0 -1.853360 -0.028105 -0.329829 6 0 1.853434 -0.028193 -0.329701 6 0 -1.275301 1.186217 -0.169709 6 0 1.275441 1.186175 -0.169349 6 0 -0.000055 1.422106 0.604685 1 0 2.034937 -2.116189 0.153530 1 0 -2.035189 -2.115861 0.154308 1 0 -2.845165 -0.059793 -0.776332 1 0 2.845303 -0.059849 -0.776054 1 0 -1.784449 2.057549 -0.569433 1 0 1.785077 2.057564 -0.568345 1 0 -0.000126 2.447442 0.983312 1 0 -0.000105 0.752055 1.472757 6 0 -0.000064 -1.624817 0.253002	177.3999 210.9575 262.8876 313.5596 401.4817 477.8907 504.3341 536.2118 701.9063 705.9780 743.3639 753.9614 790.2973 817.0937 871.6391 909.6358 943.2622 956.8894 971.6594 1036.5122 1061.2730 1140.6423 1209.0810 1247.9511 1271.4108 1310.7521 1332.4268 1381.6338 1409.0424 1424.0487 1429.5797 1483.8566 1603.1379 1628.2602 3013.2716 3069.4999 3097.0858 3100.2433 3125.0177 3126.2455 3159.7900 3163.5278	
i4 	6 0 0.000000 1.832500 -0.000000 6 0 1.832500 -0.000000 -0.000000 6 0 1.295773 -1.295773 -0.000000 6 0 -1.295773 1.295773 0.000000 6 0 -0.000000 -1.832500 0.000000 6 0 -1.832500 -0.000000 -0.000000 6 0 -1.295773 -1.295773 -0.000000 1 0 0.000000 2.919300 -0.000000 1 0 2.919300 -0.000000 -0.000000 1 0 2.064257 -2.064257 -0.000000 1 0 -2.064257 2.064257 0.000000 1 0 -0.000000 -2.919300 0.000000 1 0 -2.919300 -0.000000 -0.000000	148.0618 149.0289 331.8985 331.9445 452.5537 452.5605 600.3686 628.4301 740.8003 740.8028 758.2350 758.2358 763.8585 898.7259 899.8151 917.9721 918.0032 958.3197 958.3205 973.5268 992.5751 1211.1770 1211.4550 1304.0161 1304.0293 1363.2839 1452.1602 1469.0042 1469.0204 1498.5666 1498.5730 1569.5082 1569.8501 1702.5809 3115.9697 3120.8889 3120.8971 3135.5145 3135.6676	

	1 0 2.064257 2.064257 -0.000000 1 0 -2.064257 -2.064257 -0.000000 6 0 1.295773 1.295773 -0.000000		3151.7942	3151.8025	3161.4652
i5 	6 0 2.020350 -0.506608 0.040227 6 0 0.433800 1.638197 -0.169265 6 0 -0.969791 1.396832 0.061399 6 0 -1.840915 0.264366 0.133283 6 0 -0.233457 -1.491753 -0.328802 6 0 -1.605709 -1.073066 -0.087984 1 0 2.357348 -0.949043 -0.904281 1 0 0.626649 2.701678 -0.331915 1 0 -1.513212 2.332132 0.168866 1 0 -2.880765 0.542778 0.296039 1 0 0.031559 -1.881732 -1.312764 1 0 -2.451013 -1.746759 -0.195993 6 0 1.568198 0.901474 -0.163943 6 0 0.722504 -1.080085 0.518264 1 0 0.414709 -0.739431 1.503208 1 0 2.844840 -0.555759 0.757766		179.8043 349.9398 465.8956 702.0670 798.7918 905.5596 980.0195 1145.4173 1254.5038 1350.5018 1467.2670 1656.2376 3059.9529 3138.8252	208.7156 388.5809 557.0275 763.8722 870.8140 928.6939 1054.1886 1164.3543 1301.4629 1381.6309 1522.5444 3016.9981 3090.3116 3142.8537	261.2682 413.8813 674.6521 769.9828 879.6484 972.4380 1071.3350 1233.4743 1339.3551 1440.7585 1549.6341 3058.8405 3113.0547 3151.2672
p1 	6 0 0.466520 -1.207874 -1.282798 6 0 -0.466520 1.207874 -1.282798 6 0 -0.000000 1.924492 -0.104091 6 0 -0.000000 -1.924492 -0.104091 6 0 0.200438 1.318492 1.118549 6 0 -0.200438 -1.318492 1.118549 6 0 0.000000 -0.000000 1.621412 6 0 -0.000000 0.000000 -1.488901 1 0 1.242714 -1.645723 -1.906010 1 0 -1.242714 1.645723 -1.906010 1 0 0.072787 3.007230 -0.147417 1 0 -0.072787 -3.007230 -0.147417 1 0 0.462419 2.016869 1.911406 1 0 -0.462419 -2.016869 1.911406 1 0 0.000000 -0.000000 2.709056		162.0550 323.7634 551.4793 735.7008 819.9044 903.2436 979.2282 1162.5622 1288.2997 1443.4682 1551.6436 3116.9185 3135.4608	231.5994 433.7977 611.5109 751.6977 832.1372 969.1877 981.2413 1251.6883 1373.7356 1456.0336 1966.8832 3128.3773 3152.9946	245.5635 470.7325 637.3983 801.9095 875.5913 970.6350 1110.7879 1253.7871 1426.8330 1528.9128 3105.8125 3129.0829 3156.0729
p2 	6 0 0.326225 -1.383291 -0.466860 6 0 -0.741919 -1.222451 0.356868 6 0 0.901978 1.410895 0.145325 6 0 -1.919003 -0.496441 -0.110337 6 0 -0.396784 1.594692 -0.272679 6 0 -1.530246 0.742213 -0.446869 1 0 -0.599888 -1.300825 1.433387 1 0 -2.954293 -0.815725 -0.047221 1 0 0.156202 -1.507599 -1.534645 1 0 1.418291 2.357192 0.293637 1 0 -0.642882 2.642951 -0.442785 6 0 1.653743 -1.014434 -0.027060 1 0 2.521045 -1.666045 -0.096477 6 0 1.814412 0.287454 0.333964		148.6530 326.8161 499.9787 714.6279 807.7051 892.9053 1006.7617 1210.1646 1302.8064 1459.3787 1606.4189 3114.1743 3132.2081	198.0393 418.0699 606.4770 752.3199 817.3898 983.3972 1053.0480 1265.6197 1330.7233 1496.0961 1625.6371 3115.7661 3146.4456	253.2148 432.0069 694.5315 793.3899 854.8598 986.5726 1114.0004 1281.8491 1428.7655 1569.1003 3092.2331 3120.7597 3152.9203

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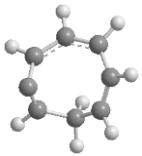
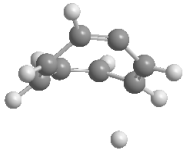
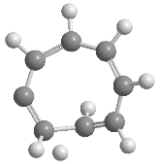
ts **i1**-**i2** 	6 0 -1.644312 -0.405102 -0.021540 6 0 -0.806472 1.433364 0.087833 6 0 0.534181 1.560217 -0.350238 6 0 1.592517 0.705914 -0.132941 6 0 0.594027 -1.561066 0.172523 6 0 1.558787 -0.641170 0.385174 1 0 -2.674096 -0.525031 -0.382954 1 0 -1.508741 2.177739 -0.288585 1 0 0.753881 2.482903 -0.882434 1 0 2.580958 1.094971 -0.365754 1 0 0.682747 -2.534824 0.642440 1 0 2.437738 -0.955759 0.943925 6 0 -1.349796 0.454151 1.024179 6 0 -0.617726 -1.315960 -0.681498 1 0 -0.325337 -0.862148 -1.640526 1 0 -1.114387 -2.259945 -0.927069	552.6851*i* 201.1393 215.6061 272.9084 305.6453 420.8391 478.4463 611.7266 630.8696 695.3294 760.3520 786.4415 821.8742 860.6170 872.4095 898.1261 945.2831 965.4775 972.9614 1006.3027 1043.0214 1150.6770 1178.4771 1204.9037 1237.9386 1250.4757 1263.7057 1330.1792 1407.0186 1428.9701 1463.6302 1472.5152 1521.0135 1633.8050 2971.1071 3006.2641 3055.3736 3086.2940 3121.0575 3129.7770 3145.6386 3166.8938
ts **i2**-**p1** 	6 0 -1.235649 -1.321686 0.180998 6 0 1.295397 -1.247934 -0.383153 6 0 1.794581 -0.051787 0.333763 6 0 1.228051 1.159416 0.363224 6 0 -1.201253 1.139357 -0.398306 6 0 0.043251 1.628591 -0.380154 1 0 -1.837068 -2.146823 0.555272 1 0 2.049749 -1.864393 -0.872833 1 0 2.728047 -0.196136 0.874393 1 0 1.740660 1.935560 0.929149 1 0 -1.943310 1.700065 -0.964003 1 0 0.208645 2.551239 -0.935146 6 0 0.040122 -1.655539 -0.364999 6 0 -1.749309 -0.062227 0.266513 1 0 -1.452011 0.475186 2.121003 1 0 -2.785863 0.016151 0.584846	982.9256*i* 156.2424 194.8703 257.6993 282.9361 305.8299 350.7909 381.1571 440.0239 618.3600 626.4766 662.4642 730.9328 778.6108 796.8201 810.8545 861.7988 900.6210 934.5241 943.0278 988.7120 1000.1830 1005.8372 1045.0037 1222.7032 1240.0082 1262.4215 1299.8102 1394.3776 1419.2273 1448.8247 1568.9488 1685.5320 1703.5606 1716.1409 3092.8973 3104.3546 3112.7591 3123.2576 3129.7834 3135.5759 3144.3035
ts **i2**-**i5** 	6 0 1.119892 -1.464941 -0.234318 6 0 1.541148 1.021412 -0.033343 6 0 0.243490 1.690034 0.108842 6 0 -1.080235 1.352619 0.014616 6 0 -1.440696 -1.145851 -0.032823 6 0 -1.831468 0.127444 -0.249280 1 0 1.114734 -2.157897 -1.066420 1 0 2.370404 1.728091 -0.020967 1 0 0.385088 2.755410 0.277798 1 0 -1.737000 2.215139 0.107313 1 0 -2.051863 -1.986452 -0.343687 1 0 -2.831202 0.291834 -0.647279 6 0 1.878464 -0.265771 -0.243187 6 0 -0.123147 -1.307079 0.581576 1 0 0.055562 -0.662279 1.436306	1964.5193*i* 172.4095 212.8337 273.1883 320.9582 398.6337 434.6949 533.7346 586.3253 683.0331 732.1420 740.3156 758.6500 810.9870 864.8179 871.5112 904.6243 949.1967 974.9028 999.0468 1015.0641 1095.7218 1124.2184 1173.7201 1222.9337 1339.9445 1343.8887 1381.2819 1383.4528 1429.0962 1469.2353 1510.5578 1601.7138 1631.7449 1985.1117 3097.1443 3109.0596 3120.8772 3138.2474 3145.3061 3165.2483 3180.8680

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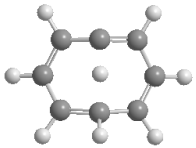
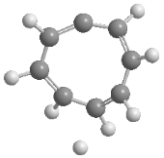
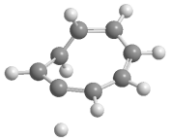
ts **i3**-**i4** 	6 0 -1.300324 -1.262810 0.003382 6 0 1.300315 -1.262815 0.003385 6 0 1.921782 -0.074656 -0.391545 6 0 -1.921784 -0.074645 -0.391544 6 0 1.322203 1.147322 -0.140430 6 0 -1.322194 1.147326 -0.140431 6 0 0.000005 1.305088 0.470842 1 0 -1.858909 -2.196161 -0.013385 1 0 1.858894 -2.196170 -0.013389 1 0 2.941849 -0.100680 -0.760033 1 0 -2.941851 -0.100660 -0.760031 1 0 1.934966 2.041836 -0.198114 1 0 -1.934949 2.041844 -0.198116 1 0 0.000001 0.054317 1.079275 1 0 0.000008 2.189310 1.117834 6 0 -0.000006 -1.213748 0.544001	1235.9901*i* 161.1582 206.9465 479.2593 479.9457 500.8535 514.6335 561.2093 588.7415 677.3650 728.7433 758.2713 768.2148 799.0296 857.0159 881.8930 957.6118 964.2532 1016.6447 1032.3724 1054.3048 1126.7055 1138.1707 1212.5723 1227.4915 1268.5661 1354.1254 1377.7600 1382.4173 1415.1966 1424.8703 1453.0093 1463.5983 1522.2520 1522.5609 3028.0162 3119.2722 3123.0903 3147.3247 3149.9555 3172.3327 3173.2248
ts **i3**-**p1** 	6 0 1.306602 -1.194498 0.469659 6 0 -1.117278 -1.394462 -0.391215 6 0 -1.802325 -0.224524 -0.219815 6 0 1.808247 -0.019739 -0.284114 6 0 -1.290976 0.966340 0.459774 6 0 1.163531 1.151971 -0.375928 6 0 -0.083450 1.579030 0.304664 1 0 1.968059 -1.650364 1.204814 1 0 -1.557072 -2.179678 -1.001353 1 0 -2.811174 -0.148213 -0.619126 1 0 2.785790 -0.107714 -0.753538 1 0 -2.026539 1.518067 1.041433 1 0 1.664451 1.951899 -0.915835 1 0 0.051333 2.493318 0.881761 6 0 0.096232 -1.647311 0.247346 1 0 -0.558346 2.821846 -1.100383	817.0972*i* 135.9328 209.9448 252.6986 263.7517 315.4424 364.9072 438.1839 474.9135 594.8832 616.5703 683.4220 706.1935 767.1426 778.5382 825.9203 879.6463 885.1486 929.3887 953.9570 958.6140 1000.4480 1007.9364 1050.9320 1194.9523 1235.7340 1259.7110 1292.2061 1392.2342 1410.0677 1446.5481 1520.3042 1604.1831 1664.6356 1781.5282 3103.6149 3107.6444 3121.2368 3123.9981 3132.7265 3143.1033 3144.9787
ts **i4**-**p2** 	6 0 0.328776 -1.402089 -0.414982 6 0 -0.716530 -1.294129 0.431630 6 0 0.860273 1.437083 -0.010370 6 0 -1.935128 -0.622953 -0.059395 6 0 -0.491849 1.576037 -0.181449 6 0 -1.626225 0.680811 -0.196253 1 0 -0.544938 -1.307772 1.506292 1 0 -2.931055 -1.038029 -0.164671 1 0 0.129003 -1.435837 -1.484818 1 0 1.365904 2.400297 -0.011817 1 0 -0.805129 2.614004 -0.285462 1 0 -2.046863 1.288952 1.567722 6 0 1.671015 -0.983694 -0.012300 1 0 2.529241 -1.647329 0.042035 6 0 1.822930 0.346307 0.179229	884.5394*i* 149.8632 189.9789 228.0337 302.7330 339.5028 379.3859 433.3882 456.4487 478.8702 606.9742 668.5585 716.8033 739.9778 777.3498 793.4810 804.7939 886.6231 915.3683 963.7065 989.0747 1004.5843 1050.4618 1098.6439 1210.9209 1242.6492 1271.4754 1317.2472 1335.2099 1416.5222 1451.0224 1532.9445 1540.0381 1602.4035 1629.3573 3101.9746 3111.5103 3119.8765 3120.7316 3136.9229 3153.2233 3165.8295

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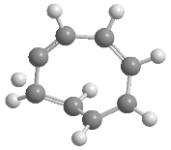
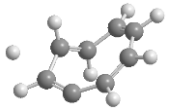
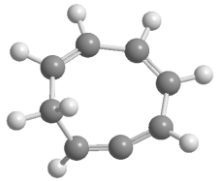
ts **i4**-**i5** 	6 0 -1.900781 -0.712805 -0.141421 6 0 -0.623791 1.562221 0.204146 6 0 0.764685 1.493395 -0.132655 6 0 1.750519 0.464401 -0.182537 6 0 0.439838 -1.524324 0.355770 6 0 1.706609 -0.890665 0.128124 1 0 -2.137818 -0.028828 1.053131 1 0 -0.897191 2.532211 0.621547 1 0 1.213593 2.482290 -0.185158 1 0 2.751681 0.862782 -0.338098 1 0 0.252257 -2.096094 1.264315 1 0 2.644613 -1.394190 0.343609 6 0 -1.694257 0.695743 0.112567 6 0 -0.563221 -1.184958 -0.491510 1 0 -0.232379 -0.705766 -1.415737 1 0 -2.872367 -1.070455 -0.458512	1783.8539*i* 255.7894 428.8496 615.2970 764.6123 832.1621 969.6971 1048.5445 1245.7430 1343.9740 1466.4908 1594.9755 3083.9368 3135.4958	166.6953 339.6239 478.0992 687.3586 790.7113 873.0001 979.4395 1090.9920 1274.4208 1364.8997 1506.0365 2106.6911 3106.2754 3151.3857	199.1734 381.4359 567.9823 740.8663 802.1503 906.7925 988.4281 1178.9186 1285.7436 1427.0851 1522.8594 3063.8088 3111.8081 3181.2150
ts **i5**-**p2** 	6 0 1.947555 -0.439714 -0.053884 6 0 0.371399 1.619330 -0.199722 6 0 -0.946620 1.391685 0.123106 6 0 -1.836592 0.238771 0.261893 6 0 -0.258929 -1.381523 -0.470720 6 0 -1.617645 -1.060090 -0.063657 1 0 2.975613 -0.779390 -0.113695 1 0 0.603451 2.678916 -0.307710 1 0 -1.496225 2.320983 0.257543 1 0 -2.852171 0.516867 0.536211 1 0 -0.054174 -1.441364 -1.538133 1 0 -2.450769 -1.756122 -0.112573 6 0 1.530315 0.798955 -0.359769 6 0 0.770919 -1.206150 0.388443 1 0 0.589877 -1.269650 1.458309 1 0 2.921995 -0.037832 2.065913	247.5588*i* 203.8371 334.6521 499.5826 722.5670 801.8595 894.5217 1006.7664 1210.5510 1312.0511 1458.1306 1604.1806 3116.6460 3135.3745	138.6740 229.5117 428.0094 617.3848 735.1197 814.0358 979.3768 1052.2601 1251.1645 1331.0051 1504.5108 1620.1781 3117.9783 3149.7166	182.4141 255.2189 441.3948 690.0555 790.4003 884.7415 987.5312 1105.4171 1275.7928 1424.3105 1566.9111 3093.6319 3134.4818 3161.6252
i2s 	6 0 -1.027071 -1.323551 -0.501240 6 0 1.414394 -1.219834 0.240586 6 0 1.905179 0.135991 0.060055 6 0 1.185156 1.281660 -0.092950 6 0 -1.428026 1.039949 0.079946 6 0 -0.228606 1.642158 -0.122131 6 0 0.220811 -1.537366 -0.223332 6 0 -1.772976 -0.375053 0.457467 1 0 -1.507577 -1.605768 -1.431253 1 0 2.043649 -1.937461 0.760406 1 0 2.986372 0.256218 0.076550 1 0 1.809922 2.161716 -0.228452 1 0 -2.288130 1.685401 -0.084122 1 0 -0.337362 2.697337 -0.366675 1 0 -1.464957 -0.601684 1.479905	101.9384 307.5236 575.0806 724.3102 832.8474 902.0386 1005.0733 1130.9095 1289.4130 1445.2781 1493.5349 1987.1002 3103.7374 3137.1934	241.2124 403.8603 595.8497 770.7804 869.0281 953.2430 1016.0428 1198.1727 1305.5538 1448.0918 1589.2023 3047.3414 3117.9590 3145.7949	256.6913 466.9868 651.8875 799.7970 890.3485 993.6480 1060.0627 1274.0878 1352.8010 1479.3186 1652.4546 3085.5970 3131.2707 3169.5528

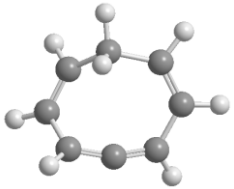
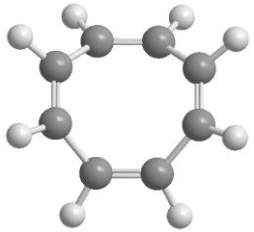
	1 0 -2.855087 -0.519489 0.403245		
i3s 	6 0 1.000113 -1.451398 -0.285141 6 0 -1.428351 -1.049852 0.486524 6 0 -1.861257 0.081882 -0.363898 6 0 1.897891 -0.295593 -0.134161 6 0 -1.082146 1.172636 -0.458173 6 0 1.504185 0.966770 0.093445 6 0 0.108268 1.489191 0.436458 6 0 -0.208697 -1.456521 0.225519 1 0 1.317748 -2.253486 -0.947988 1 0 -2.038801 -1.430581 1.300939 1 0 -2.782989 0.015226 -0.937527 1 0 2.954378 -0.475012 -0.313397 1 0 -1.368567 1.951273 -1.161251 1 0 2.283787 1.723366 0.109245 1 0 0.182186 2.578487 0.495071 1 0 -0.127778 1.148034 1.451469	150.8039 227.6670 253.3731 302.2531 414.2074 454.4968 526.5034 559.5041 679.6499 713.5968 753.3316 785.7746 808.3978 866.5504 871.6061 942.7173 976.3278 987.9181 992.3921 998.4964 1053.7859 1119.3402 1213.9342 1252.2659 1267.9472 1289.9544 1354.6229 1394.7698 1417.7238 1435.6499 1478.3645 1652.9359 1665.5998 1981.9330 3012.3382 3059.2858 3120.2840 3121.7685 3134.3819 3135.3918 3146.1354 3157.1023
i4s 	6 0 0.375710 -1.564202 0.669220 6 0 0.375652 -1.564301 -0.669060 6 0 0.375595 1.564311 0.669069 6 0 -0.375670 -0.669221 -1.564212 6 0 0.375686 1.564212 -0.669211 6 0 -0.375613 0.669059 -1.564311 1 0 0.930905 -2.355212 -1.171197 1 0 -0.930949 -1.171437 -2.355054 1 0 0.931009 -2.355031 1.171437 1 0 0.930977 2.355055 -1.171414 1 0 -0.930847 1.171197 -2.355235 6 0 -0.375634 -0.669069 1.564301 1 0 -0.930874 -1.171221 2.355212 1 0 0.930816 2.355236 1.171220 6 0 -0.375726 0.669211 1.564203 1 0 -0.931037 1.171413 2.355031	179.1433 233.8262 263.8547 291.9058 363.6961 363.6961 649.9608 649.9608 673.1933 683.7027 775.0243 812.5860 812.5860 887.8073 941.3255 957.4068 957.4068 980.9307 1002.8831 1002.8831 1012.1621 1047.1945 1238.3034 1240.7181 1254.9157 1254.9157 1387.8830 1431.4549 1431.4549 1469.4725 1694.9738 1694.9738 1699.9728 1717.7148 3100.8922 3104.3945 3104.3945 3110.0730 3120.9842 3128.2777 3128.2777 3135.1456

Table S2. Calculated Branching Ratios of Various Channels in the C_7H_8 Reaction

	Collision Energy, kJ mol^{-1}														
	0			**10**			**20**			**32**			**40**		
	from **i1**	from **i3**	2/3 **i1**, 1/3 **i3**	from **i1**	from **i3**	2/3 **i1**, 1/3 **i3**	from **i1**	from **i3**	2/3 **i1**, 1/3 **i3**	from **i1**	from **i3**	2/3 **i1**, 1/3 **i3**	from **i1**	from **i3**	2/3 **i1**, 1/3 **i3**
p1 from **i2**	100.00	0.00	66.67	100.00	0.00	66.66	99.99	0.00	66.66	99.99	0.00	66.66	99.99	0.00	66.66
p1 from **i3**	0.00	2.04	0.68	0.00	2.49	0.83	0.00	2.99	1.00	0.00	3.65	1.22	0.00	4.16	1.39
p1 from **i4**	0.00	97.96	32.66	0.00	97.51	32.51	0.00	97.01	32.34	0.01	96.35	32.12	0.01	95.84	31.95
p2 from **i4**	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
p2 from **i5**	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

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