Table S1. Optimum geometric structures (Å or deg) of *o*-benzyne at various levels of theory[a]

	r_1	r_2	r_3	r_4	r_5	r_6	θ_1	θ_2	θ_3	θ_4	θ_5
HF / cc-pVDZ	1.4119	1.3942	1.3866	1.2272	1.0833	1.0798	122.60	109.93	127.47	118.45	127.19
HF / cc-pVTZ	1.4075	1.3877	1.3807	1.2160	1.0744	1.0704	122.54	109.88	127.58	118.45	127.18
MP2 / cc-pVDZ	1.4197	1.4165	1.4008	1.2801	1.0965	1.0940	122.73	110.64	126.63	118.72	126.94
MP2 / cc-pVTZ	1.4071	1.4055	1.3866	1.2622	1.0828	1.0798	122.68	110.48	126.84	118.75	127.04
CCSD / cc-pVDZ	1.4221	1.4150	1.4019	1.2670	1.0968	1.0939	122.53	110.73	126.74	118.63	126.69
CCSD / cc-pVTZ	1.4092	1.4019	1.3871	1.2472	1.0819	1.0786	122.51	110.52	126.98	118.63	126.83
CCSD(T) / cc-pVDZ	1.4235	1.4218	1.4055	1.2800	1.0987	1.0959	122.48	111.06	126.46	118.75	126.48
CCSD(T) / cc-pVTZ	1.4106	1.4093	1.3906	1.2603	1.0840	1.0808	122.47	110.80	126.73	118.75	126.66
c~CCSD(T)-AE / cc-pCVQZ	1.4048	1.4035	1.3846	1.2539	1.0819	1.0788	122.46	110.78	126.76	118.77	126.72

[a] See text figures for coordinate labels.

Table S2. Optimum geometric structures (Å or deg) of the (C_{2v}) retro-Diels Alder transition state for *o*-benzyne fragmentation at various levels of theory[a]

	r_1	r_2	r_3	r_4	r_5	r_6	θ_1	θ_2	θ_3	θ_4	θ_5
HF / cc-pVDZ	1.2342	2.1487	1.2346	1.3324	1.0679	1.0684	117.98	101.06	140.96	149.28	152.89
HF / cc-pVTZ	1.2246	2.1325	1.2241	1.3220	1.0583	1.0582	118.03	100.82	141.15	148.67	153.22
MP2 / cc-pVDZ	1.2640	2.2209	1.2718	1.3507	1.0797	1.0830	117.81	100.88	141.32	152.62	151.68
MP2 / cc-pVTZ	1.2475	2.2046	1.2538	1.3334	1.0655	1.0680	117.90	100.06	142.04	152.70	153.00
CCSD / cc-pVDZ	1.2589	2.1972	1.2630	1.3556	1.0814	1.0832	117.86	101.36	140.78	150.78	151.69
CCSD / cc-pVTZ	1.2411	2.1712	1.2437	1.3370	1.0658	1.0669	117.95	100.83	141.23	150.63	152.76
CCSD(T) / cc-pVDZ	1.2643	2.2327	1.2712	1.3594	1.0831	1.0854	117.69	101.17	141.14	151.64	151.22
CCSD(T) / cc-pVTZ	1.2466	2.2068	1.2518	1.3410	1.0676	1.0692	117.81	100.51	141.69	151.67	152.59
c~CCSD(T)-AE / cc-pCVQZ	1.2409	2.1975	1.2457	1.3350	1.0659	1.0673	117.84	100.35	141.81	151.50	152.98

[a] See text figures for coordinate labels.

Table S3. Optimum geometric structures (Å) of acetylene and diacetylene at various levels of theory[a]

	Diacetylene			Acetylene	
	r_1	r_2	r_3	r_1	r_2
HF / cc-pVDZ	1.0637	1.1936	1.3920	1.0639	1.1918
HF / cc-pVTZ	1.0538	1.1822	1.3850	1.0540	1.1801
MP2 / cc-pVDZ	1.0762	1.2372	1.3842	1.0755	1.2297
MP2 / cc-pVTZ	1.0620	1.2194	1.3687	1.0615	1.2114
CCSD / cc-pVDZ	1.0777	1.2258	1.3984	1.0776	1.2228
CCSD / cc-pVTZ	1.0620	1.2067	1.3821	1.0620	1.2033
CCSD(T) / cc-pVDZ	1.0793	1.2336	1.3953	1.0790	1.2287
CCSD(T) / cc-pVTZ	1.0639	1.2150	1.3789	1.0637	1.2097
c~CCSD(T)-AE / cc-pCVQZ	1.0620	1.2093	1.3741	1.0620	1.2038
CCSD(T)-AE / cc-pCVQZ	1.0621	1.2091	1.3742	1.0621	1.2037

[a] See text figures for coordinate labels.

Table S4. CCSD(T)/cc-pVDZ vibrational frequencies along the retro-Diels-Alder fragmentation path of *o*-benzyne

mode	*o*-benzyne	transition state	products
$\omega_1(a_1)$	3220	3412	3500 (σ_g C_2H_2)
$\omega_2(a_1)$	3195	3369	3454 (σ_g C_4H_2)
$\omega_3(a_1)$	1881	1995	2215 (σ_g C_4H_2)
$\omega_4(a_1)$	1474	1742	1986 (σ_g C_2H_2)
$\omega_5(a_1)$	1324	1106	885 (σ_g C_4H_2)
$\omega_6(a_1)$	1147	832	734 (π_u C_2H_2)
$\omega_7(a_1)$	1054	686	584 (π_u C_4H_2)
$\omega_8(a_1)$	995	391	220 (π_u C_4H_2)
$\omega_9(a_1)$	599	615*i*	0
$\omega_{10}(a_2)$	925	595	598 (π_g C_4H_2)
$\omega_{11}(a_2)$	848	553	527 (π_g C_2H_2)
$\omega_{12}(a_2)$	551	447	453 (π_g C_4H_2)
$\omega_{13}(a_2)$	413	245	0
$\omega_{14}(b_1)$	896	650	734 (π_u C_2H_2)
$\omega_{15}(b_1)$	734	597	584 (π_u C_4H_2)
$\omega_{16}(b_1)$	379	218	220 (π_u C_4H_2)
$\omega_{17}(b_2)$	3217	3370	3455 (σ_u C_4H_2)
$\omega_{18}(b_2)$	3178	3353	3410 (σ_u C_2H_2)
$\omega_{19}(b_2)$	1494	1833	2034 (σ_u C_4H_2)
$\omega_{20}(b_2)$	1411	813	598 (π_g C_4H_2)
$\omega_{21}(b_2)$	1249	710	527 (π_g C_2H_2)
$\omega_{22}(b_2)$	1101	466	0
$\omega_{23}(b_2)$	840	414	453 (π_g C_4H_2)
$\omega_{24}(b_2)$	455	93*i*	0