Supporting Information

UV Photochemistry of Benzene and Cyclohexadienyl Radical in Solid Parahydrogen

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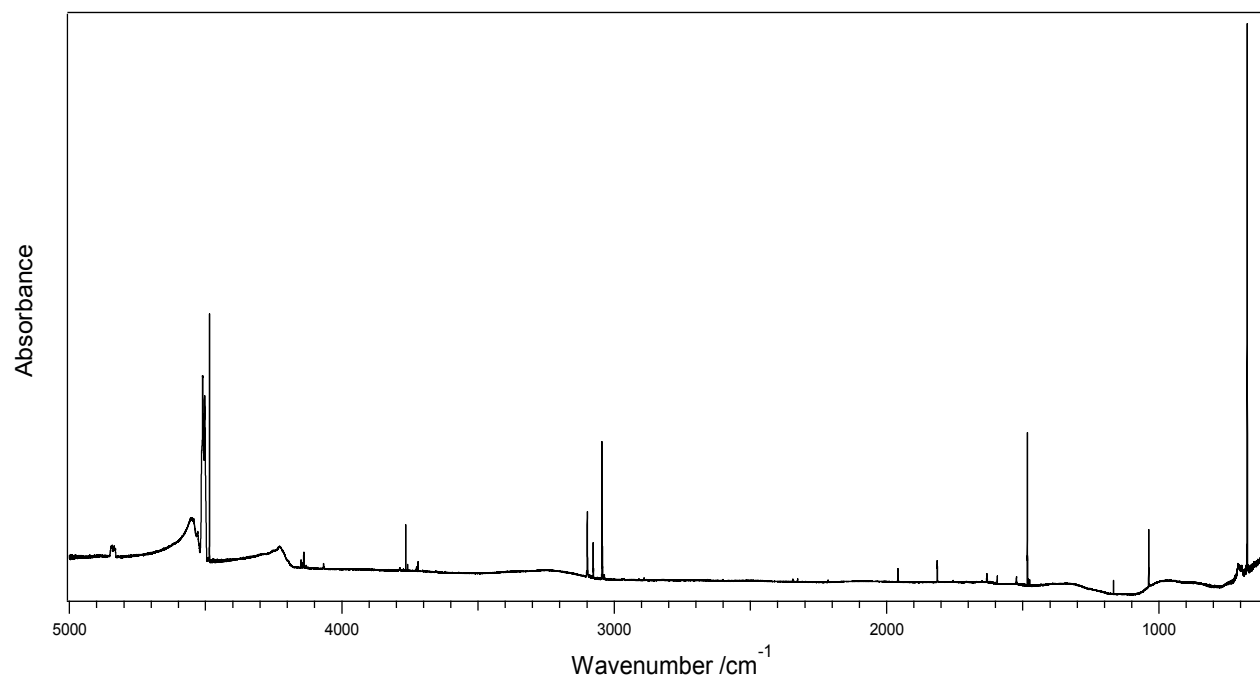
Figure S1. Full spectrum of benzene (25ppm) embedded in solid parahydrogen at 4.2K immediately after deposition.
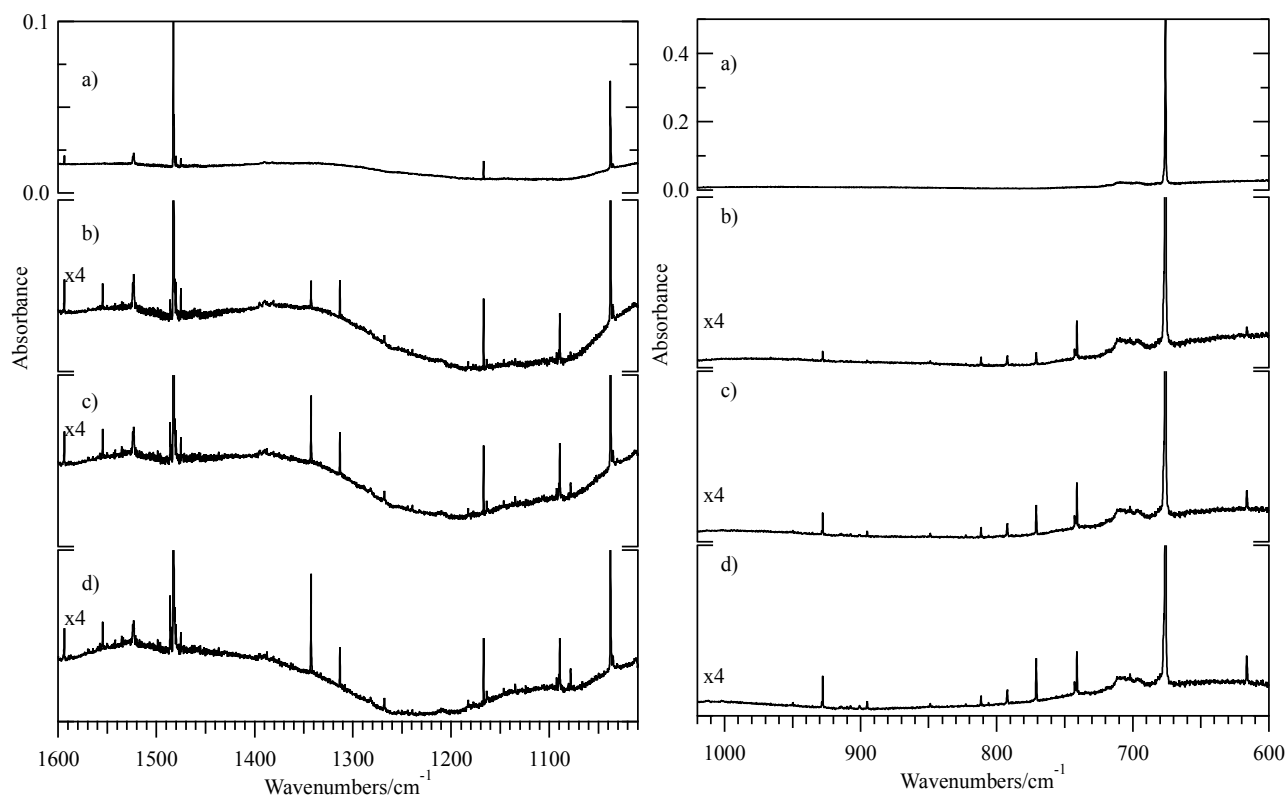
Figure S2. 193 nm ArF excimer laser irradiation of Benzene in solid parahydrogen at 4.2K: IR region of 1600 – 1010 cm^{-1} (left panel) and 1020 – 600 cm^{-1} (right panel). (a) Benzene in solid parahydrogen just after deposition, (b) after 5 minutes irradiation, (c) after 15 minutes irradiation, (d) after 30 minutes irradiation.
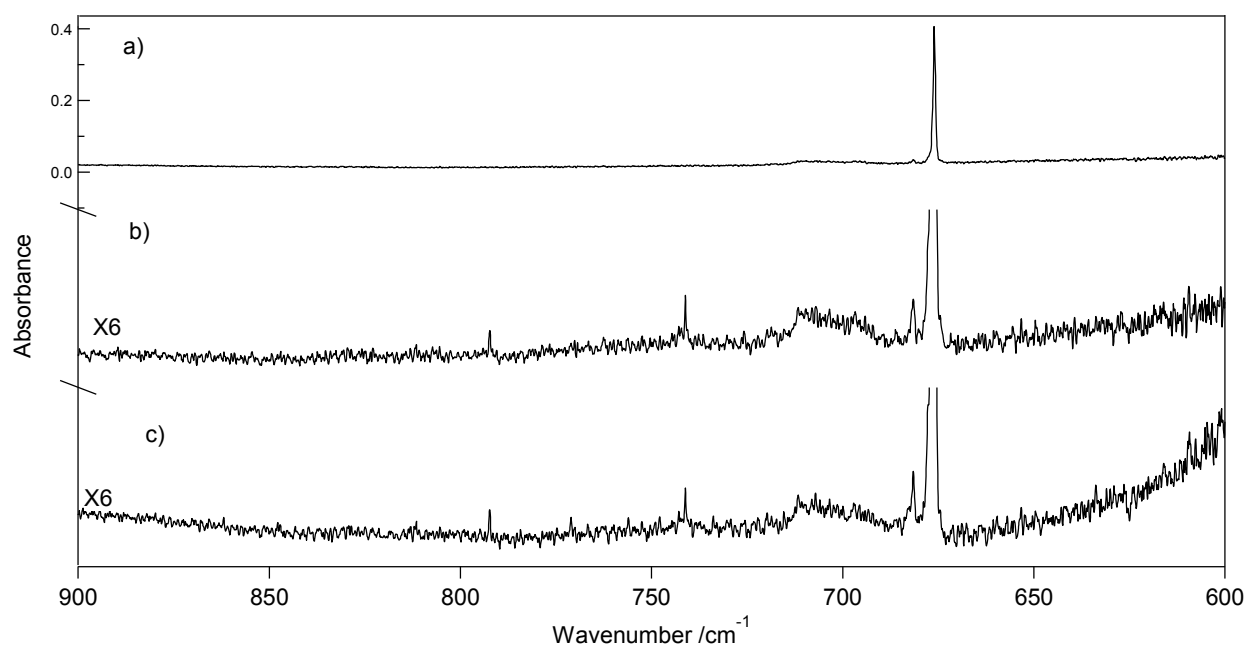
Figure S3. 253.7 nm Hg vapour lamp irradiation on Benzene in solid parahydrogen at 4.2K: IR region of 900 - 600 cm^{-1}. (a) Benzene in solid parahydrogen just after deposition, (b) after 7.5 hours irradiation, (c) after 15 hours irradiation.

Table S1. Experimental and calculated vibrational wavenumbers of benzene in solid parahydrogen compared with those in Ar and N_2 matrices.

Observed /parahydrogen [cm^{-1}]	Relative intensity	Observed / Ar matrix [a] [cm^{-1}]	Observed / N_2 matrix [b] [cm^{-1}]	Calculated [cm^{-1}] [c]	Calculated relative intensity [d]	Sym. in D_{6h}	Mode	Assignment
				410.691	0	E_{2u}		
		606		622.183	0	E_{2g}	ν_{18}	$E_{2g}\ \delta(CC)$
676.1	1.000	676	678.6	687.291	1.00	A_{2u}	ν_4	$A_{2u}\ \pi(CH)$
				718.975	0	B_{2g}		
		847		862.855	0	E_{1g}	ν_{11}	$E_{1g}\ \pi(CC)$
		967		987.207	0	E_{2u}	ν_{19}	$E_{2u}\ \pi(CH)$
		993					ν_7	$B_{2g}\ \pi(CH)$
				1010.631	0	A_{1g}		
				1017.130	0	B_{2g}		
		1010	1009.1	1022.335	0	B_{1u}	ν_6	$B_{1u}\ \nu(CC)$
			1038.1					
1038.1	0.52	1041	1039.8	1058.654	0.051	E_{1u}	ν_{14}	$E_{1u}\ \delta(CH)$
		1149		1174.449	0	B_{2u}	ν_{10}	$B_{2u}\ \delta(CH)$
1177.5	0.001	1180	1180	1197.095	0	E_{2g}	ν_{17}	$E_{2g}\ \delta(CH)$
1245.4	0.0004	1246	1248.2				$\nu_{11}+\nu_{20}$	$E_{1g}\ \pi(CC) + E_{2u}\ \pi(CC)$
1246.6	0.0006							
			1391.6					
				1335.640	0	B_{2u}		
				1380.919	0	A_{2g}		
1390.1	0.002	1390	1392.6				$\nu_7+\nu_{20}$	$B_{2g}\ \pi(CH) + E_{2u}\ \pi(CC)$
1482.9	0.27	1483	1482.9				ν_{13}	$B_{2u}\ \nu(CC)$
				1509.963	0.057	E_{1u}		
1523.1	0.013	1521	1527.6				$\nu_4+\nu_{11}$	$A_{2u}\ \pi(CH) + E_{1g}\ \pi(CC)$
1524.3	0.009							
			1589.1	1633.085	0	E_{2g}	ν_{16}	$E_{2g}\ \nu(CC)$
			1607.4				$\nu_2+\nu_{18}$	$A_{1g}\ \nu(CC) + E_{2g}\ \delta(CC)$
1620.6	0.003	1620	1619.8				$\nu_6+\nu_{18}$	$B_{1u}\ \nu(CC) + E_{2g}\ \delta(CC)$
1669.1	0.002	1670	1671.1				$\nu_8+\nu_{19}$	$B_{2g}\ \pi(CC) + E_{2u}\ \pi(CH)$
			1713.8				$\nu_8+\nu_6$	$B_{2g}\ \pi(CC) + E_{1u}\ \nu(CC)$
1755.7	0.003	1759	1757.9				$\nu_{10}+\nu_{18}$	$B_{2u}\ \delta(CH) + E_{2g}\ \delta(CC)$
1813.5	0.039	1812	1816.9				$\nu_{11}+\nu_{19}$	$E_{1g}\ \pi(CC) + E_{2u}\ \pi(CH)$
1814.2	0.027							
1958.2	0.024	1956	1961				$\nu_7+\nu_{19}$	$B_{2g}\ \pi(CH) + E_{2u}\ \pi(CH)$
1958.8	0.022							
2214.2	0.003		2217				$\nu_{14}+\nu_{17}$	$E_{1u}\ \delta(CH)+E_{2g}\ \delta(CH)$
2600.6	0.002	2600	2598.6				$\nu_6+\nu_{16}$	$B_{1u}\ \nu(CC) + E_{2g}\ \nu(CC)$
								$A_{1g}\ \nu(CC) + E_{2g}\ \delta(CC)$
2619.2	0.001		2617				$\nu_2+\nu_{18}+\nu_6$	$+ B_{1u}\ \nu(CC)$
2657.3	0.001							
2819.2	0.001		2820.5					
2826.7	0.002	2827	2828.7				$\nu_3+\nu_{13}$	$A_{2g}\ \delta(CH) + B_{2u}\ \nu(CC)$
			2855.1					
2890.3	0.004	2890	2889.4				$\nu_9+\nu_{16}$	$B_{2u}\ \nu(CC) + E_{2g}\ \nu(CC)$
								$A_{1g}\ \nu(CC) + E_{2g}\ \delta(CC)$
2909.2	0.002	2910	2908.4				$\nu_2+\nu_{18}+\nu_9$	$+ B_{2u}\ \nu(CC)$
3036.2	0.007							
				3155.447	0	B_{1u}		
				3165.079	0	E_{2g}		

3037.0	0.004							
3038.1	0.006							
3042.8	0.063							
3044.8	0.246	3047	3044	3180.665	0.30	E_{1u}	ν_{12}	$E_{1u}\ \nu(CH)$
3045.7	0.091							
3076.0	0.021							
								$E_{1u}\ \nu(CC) + A_{1g}\ \nu(CC)$
3077.2	0.063	3079	3077				$\nu_{13}+\nu_2+\nu_{18}$	$+ E_{2g}\ \delta(CC)$
3077.7	0.032							
3082.8	0.003							
3096.9	0.039							
3098.3	0.117							
3098.9	0.068	3100	3099				$\nu_{13}+\nu_{16}$	$E_{1u}\ \nu(CC) + E_{2g}\ \nu(CC)$
3100.1	0.006							
3101.1	0.010							
				3190.846	0	A_{1g}		

[a] Andrews, L.; Johnson, G.L.; Davis, S.R. Infrared spectrum of the benzene-hydrogen fluoride complex in solid argon. *J. Phys. Chem*. **1985**, 89, 1706-1709.

[b] Fredin, L.; Nelander, B. On the structure of benzene halogen complexes. A matrix isolation study. *Mol. Phys*. **1974**, 27, 885-898.

[c] Vibrational wavenumbers of benzene were calculated with the B3LYP/6-311+G (d, p) method.

[d] Relative intensities were normalized to the most intense benzene band at 687.291 cm^{-1}, which was calculated to be 125.03 km/mol with B3LYP/6-311+G(d, p).

Table S2. Experimental and calculated vibrational wavenumbers of benzvalene in solid parahydrogen compared with those in Ar and N_2 matrices.

Observed /parahydrogen [cm⁻¹]	Relative intensity	Observed / Ar matrix [a] [cm⁻¹]	Observed / N₂ matrix [a] [cm⁻¹]	Calculated [cm⁻¹] [b]	Calculated relative intensity [c]	Sym. in C₂ᵥ	Mode	Assignment [d]
		505 s	508 s	509.270	0.142	B₁	v_{22}	C-C-C=C torsion
		534 vvw	534 vvw	543.408	0	A₂	v_{16}	C-C-C=C torsion
		632 w	635 w	632.624	0.006	B₁	v_{21}	C-H wag
		653 m	651 m	690.007	0.055	A₁	v_{11}	C-H wag
741.1	1	741 vvs	744 vvs	756.242	1.000	B₁	v_{20}	C-H wag [e]
742.8	0.34	744 vvs	747 vvs					
		756 mw	757 mw					
760.4	0.03	762 mw	763 mw	762.116	0.031	A₁	v_{10}	C-H wag
				764.870	0	A₂	v_{15}	C-C stretch
		801 vw	802 vw					C-C stretch
811.6	0.24	812 s	812 s	824.743	0.124	B₂	v_{30}	C-C=C bend
		841 vvw						
849.1	0.11	849 ms	850 ms	861.344	0.035	B₂	v_{29}	C-H wag
				896.153	0.004	A₁	v_9	C-C stretch
				899.998	0	A₂	v_{14}	C-H wag
				920.360	0	A₂	v_{13}	C-H wag
		875 vw						
		882 w	881 w					
		902 w	907 w					
		970 w	972 w					
		979 vw	982 w					
				982.612	0.003	B₂	v_{28}	C-H wag
				987.669	0.002	A₁	v_8	C-H wag
				996.859	0.001	B₁	v_{19}	C-H wag
		1014 vvw	1017 vvw				$2v_{22}$	
		1022 vvw						
		1063 vw	1065 vw				$2v_{16}$	
1089.5	0.28	1088 vs		1112.676	0.291	B₁	v_{18}	C-C stretch
1090.4	0.09	1090 vs	1090 vs	1113.769	0.034	A₁	v_7	C-H wag
1092.7	0.05	1094 vs		1116.450	0	A₂	v_{12}	C-H wag
			1097 w					
1163.8	0.06	1163 m	1163 ms	1192.789	0.038	A₁	v_6	C-H wag
1182.7	0.04	1182 mw	1183 m	1201.496	0.030	B₂	v_{27}	C-C stretch
1239.6	0.02	1240 mw	1240 m	1267.418	0.021	B₂	v_{26}	C-C stretch
		1260 vvw						
		1276 vvw	1279 vw					
			1293 vvw					
		1304 vw	1305 w					
1313.3	0.20	1312 m	1314 s	1334.807	0.059	B₂	v_{25}	C-C stretch
		1342 vw	1343 vw					
		1358 vw	1360 w					
		1380 w	1385 w					
			1395 vw					
		1413 vvw	1415 vvw					
		1505 w	1513 w					

		1523 vw						
				1404.256	0.001	A_1	ν_5	C-C stretch
1554.8	0.13	1554 m	1553 m	1609.252	0.081	A_1	ν_4	C=C stretch
			1618 w					
				3181.755	0.006	A_1	ν_3	C-H stretch
3066.2	0.01	3067 m		3183.864	0.240	B_2	ν_{24}	C-H stretch
3071.6	0.04		3072 s					
		3077 m		3207.370	0.119	A_1	ν_2	C-H stretch
		3082 m		3187.904	0.140	B_1	ν_{17}	C-H stretch
				3214.081	0.059	B_2	ν_{23}	C-H stretch
		3095 w	3092 s	3238.359	0.065	A_1	ν_1	C-H stretch
		3128 w	3128 w				$2\nu_4$	

[a] Griffith, D.W.T.; Kent, J.E.; O'Dwyer, M.F. The vibrational spectra of Dewar benzene and benzvalene. *Aust. J. Chem.* **1975**, 28, 1397-1416.

[b] Vibrational wavenumbers of benzvalene were calculated with the B3LYP/6-311+G (d, p) method.

[c] Relative intensities were normalized to the most intense benzvalene band at 756.242 cm^{-1}, which was calculated to be 102.941 km/mol with B3LYP/6-311+G(d, p).

[d] Jensen, J. O. Vibrational frequencies and structural determination of benzvalene. *J. Mol. Struct. THEOCHEM.* **2003**, 634, 41-52

[e] The ν_{20} was assigned using our DFT calculation result

Table S3. Experimental and calculated vibrational wavenumbers of Dewar benzene in solid parahydrogen compared with those in Ar matrix.

Observed /parahydrogen [cm^{-1}]	Relative intensity	Observed / Ar matrix [a) [cm^{-1}]	Calculated [cm^{-1}] [b)	Calculated relative intensity [c)	Sym. in C$_{2v}$	Mode	Assignment[d)
		390 m	339.411	0	A$_2$	ν_{16}	C-C-C-C torsion
		394 w	388.944	0.068	A$_1$	ν_9	C-C-C bend
		488 m	487.477	0.059	B$_2$	ν_{30}	C-C-C-C torsion
		491 m					
702.2	0.47	705 vs	718.606	0.593	B$_1$	ν_{22}	C-H wag
		709 vs					
		741 vw					
		743 vw					
		780 w					
			790.878	0	A$_2$	ν_{15}	C-C-C bend
792.3	1	793 vvs	811.375	1.0	A$_1$	ν_8	C-H wag
		795 vvs					
		811 vw					
822.9	0.22	823 s	830.375	0.146	B$_2$	ν_{29}	C-C stretch
		826 s					
		842 vw					
		878 vw					
			863.297	0.001	A$_1$	ν_7	C-C stretch
			933.438	0	A$_2$	ν_{14}	C-H wag
923.3	0.08	923 m	937.552	0.073	B$_2$	ν_{28}	C-C-C bend
928.8	0.41	928 ms	940.964	0.100	A$_1$	ν_6	C-C stretch
			953.247	0	A$_2$	ν_{13}	C-C stretch
935.4	0.09	936 ms	967.688	0.031	B$_2$	ν_{27}	C-H wag
		938 ms					
		983 vw					
		987 vw					
		1012 mw					
		1015 mw					
		1020 mw					
		1079 mw					
		1083 mw					
		1089 w					
		1133 ms					
			992.672	0.004	B$_1$	ν_{21}	C-C stretch
			1032.512	0.026	A$_1$	ν_5	C-H wag
			1094.159	0.007	B$_1$	ν_{20}	C-H wag
1134.8	0.11	1135 ms	1158.621	0.088	B$_2$	ν_{26}	C-H wag
1146.8	0.04	1147 ms	1173.478	0.060	A$_1$	ν_4	C-H wag
		1149 ms					
		1181 w					
			1198.833	0	A$_2$	ν_{12}	C-H wag
			1199.995	0.021	B$_1$	ν_{19}	C-H wag
		1259 vw					
			1280.125	0	A$_2$	ν_{11}	C-H wag
1268.1	0.16	1268 s	1292.309	0.463	B$_2$	ν_{25}	C-H wag
		1270 s					
1282.1	0.07	1281 m					
		1284 m					
		1312 w					

		1317 w					
		1515 vw					
1535.5	0.10	1536 ms	1590.753	0.177	B_1	ν_{18}	C=C stretch
		1539 ms					
		1615 w					
		1716 vw					
		2963 m					
		2968 w					
		2973 m					
		2983 m					
			1617.585	0.002	A_1	ν_3	C=C stretch
2984.7	0.05	2986 vs	3090.070	0.197	B_2	ν_{24}	C-H stretch
		2992 w					
		3000 w					
		3005 w					
		3038 vs					
3048.8	0.10	3046 s	3096.486	0.375	A_1	ν_2	C-H stretch
		3053 w					
3058.8	0.07						
		3061 w					
		3064 m					
3069.6	0.15	3069 m					
		3074 w					
		3077 m					
		3088 w					
		3090 w					
			3169.273	0	A_2	ν_{10}	C-H stretch
3107.8	0.06	3107 m					
3108.9	0.05						
3110.9	0.15	3112 m	3170.904	0.314	B_2	ν_{23}	C-H stretch
3111.5	0.12		3200.019	0.463	B_1	ν_{17}	C-H stretch
		3118 w					
		3127 w					
3133.6	0.06	3134 w	3202.731	0.106	A_1	ν_1	C-H stretch

[a] Griffith, D.W.T.; Kent, J.E.; O'Dwyer, M.F. The vibrational spectra of Dewar benzene and benzvalene. *Aust. J. Chem.* **1975**, 28, 1397-1416.

[b] Vibrational wavenumbers of Dewar benzene were calculated with the B3LYP/6-311+G (d, p) method.

[c] Relative intensities were normalized to the most intense Dewar benzene band at 811.375 cm^{-1}, which was calculated to be 84.547 km/mol with B3LYP/6-311+G(d, p).

[d] Jensen, J. O. Vibrational frequencies and structural determination of benzvalene. *J. Mol. Struct. THEOCHEM.* **2003**, 634, 41-52

Table S4. Experimental and calculated vibrational wavenumbers of fulvene in solid parahydrogen compared with those in Ar matrix.

Observed /parahydrogen [cm⁻¹]	Relative intensity	Observed / Ar matrix [a] [cm⁻¹]	Calculated [cm⁻¹] [b]	Calculated relative intensity [c]	Sym. in C_{2v}	Mode	Assignment
		350 m	209.868	0.090	B_1	ν_{20}	ring torsion
			345.140	0.008	B_2	ν_{30}	methylene in-phase bend
		494 m	491.367	0	A_2	ν_{15}	ring torsion
616.4	0.58	613 vs	633.989	0.898	B_1	ν_{19}	C-H out-of-plane
		666 w					
			678.718	0.001	A_1	ν_{11}	ring in-plane deform
			690.893	0	A_2	ν_{14}	C-H out-of-plane + CH2 torsion
			777.279	0	A_2	ν_{13}	C-H out-of-plane + CH2 torsion
771.0	1.0	769 s	788.812	1.00	B_1	ν_{18}	C-H out-of-plane
		795 w	807.262	0.015	B_2	ν_{29}	ring deform + C-C stretch
895.3	0.16	894 m	908.709	0.166	A_1	ν_{10}	C-C-C stretch
907.5	0.06	907 m	932.929	0.024	B_1	ν_{17}	C-H out-of-plane
			943.648	0	A_2	ν_{12}	C-H out-of-plane
			961.584	0.071	B_2	ν_{28}	CH2 wag
927.9	0.74	926 s	965.571	0.722	B_1	ν_{16}	CH2 out-of-plane
949.9	0.07	952 m	998.903	0.043	A_1	ν_9	C-C stretch
		986 m					
			1101.775	0.034	A_1	ν_8	C-H in-plane bent
1078.5	0.09	1077 m	1104.137	0.176	B_2	ν_{27}	C-H in-plane bent
		1082 w					
		1130 w					
			1252.448	0.011	B_2	ν_{26}	C-H in-plane + CH2 in-plane
			1332.474	0.006	B_2	ν_{25}	C-H in-plane + C-C stretch
1342.6	0.46	1342 s	1367.0888	0.431	A_1	ν_7	C-H in-plane
		1372 vw					
		1391 w					
		1449 m					
			1451.554	0.001	A_1	ν_6	CH2 wag
1485.5	0.12	1486 s	1525.247	0.602	A_1	ν_5	ring C=C sym stretch
1486.1	0.25						
		1632 vw					
			1609.160	0.005	B_2	ν_{24}	ring C=C anti-sym stretch
			1695.179	0.030	A_1	ν_4	methlene C=C stretch
3007.6	0.03	3008 s	3135.820	0.109	A_1	ν_3	methylene C-H stretch
		3051 w	3197.384	0.051	B_2	ν_{23}	ring C-H stretch
		3075 mw	3207.088	0.134	A_1	ν_2	ring C-H stretch
3088.0	0.05	3088 m	3221.422	0.117	B_2	ν_{22}	CH2 C-H stretch
3088.9	0.03		3224.270	0.202	B_2	ν_{21}	ring C-H stretch
3104.7	0.01	3104 w	3230.016	0.0578	A_1	ν_1	ring C-H stretch

[a] Griffith, D.W.T.; Kent, J.E.; O'Dwyer, M.F. The vibrational spectra of Dewar benzene and benzvalene. *Aust. J. Chem.* **1975**, 28, 1397-1416.

[b] Vibrational wavenumbers of fulvene were calculated with the B3LYP/6-311+G (d, p) method.

[c] Relative intensities were normalized to the most intense fulvene band at 788.812 cm⁻¹, which was calculated to be 50.061 km/mol with B3LYP/6-311+G(d, p).

Table S5. Experimental and calculated vibrational wavenumbers of 3-cis-1,3,5-Hexatriene in solid parahydrogen compared with those in Ar matrices.

Observed/ parahydrogen [cm⁻¹]	Relative Intensity	Calculated [cm⁻¹] [a]	Relative Intensity [b]	Observed/ Ar matrix [cm⁻¹] [c]		Observed/ Ar matrix [cm⁻¹] [d]	
		102.57	0.00				
		156.11	0.00				
		163.01	0.00				
		332.23	0.00				
		351.63	0.11				
		394.93	0.00	350	w		
		601.31	0.30	605	s	588	s
		688.84	0.00				
		729.97	0.00				
		843.64	0.02	820	w	817	m
		892.93	0.00				
		931.96	0.00				
907.9	1	935.79	1.00	910	vs	906	vs
		964.97	0.04	950	w	950	m
		983.28	0.00				
990.6	0.22	1023.75	0.33	990	s	987	vs
		1036.43	0.00				
		1101.35	0.01	1015	m		
		1212.41	0.03	1190	w	1186	m
		1285.47	0.00	1235	w	1277	w
		1308.77	0.00	1325	w	1316	m
		1343.21	0.04	1365	w	1357	m
		1388.88	0.00	1460	m	1452	s
		1434.11	0.01	1605	sh		
		1487.21	0.08	1610	m	1610	m
		1616.47	0.00	1630	w	1620	m
		1672.22	0.22				
		1682.06	0.00				
				1825	w	1812	s
				3010	w	2983	w
		3126.70	0.00				
		3132.37	0.02	3030	w	3002	w
		3133.36	0.09	3035	w	3025	m
		3146.25	0.00				
		3148.47	0.08				
		3160.76	0.22	3060	m	3047	m
		3221.25	0.00	3103	w	3074	vw
		3221.74	0.24	3110	m	3101	m

a) Vibrational wavenumbers of 3-cis-1,3,5-hexatriene were calculated with B3LYP/6-311+G(d,p) method.

b) Relative intensities were normalized to the most intense band of 935.7901 cm⁻¹ of 3-cis-1,3,5-hexatriene which was calculated to be 107.68 km/mol with B3LYP/6-311+G(d,p)

c) Datta, P.; Goldfarb , T.D.; Boikess, R.S. Photolysis of Matrix Isolated 1,3-Cyclohexadiene, cis-l,3,5-Hexatriene, and trans-l,3,5-Hexatriene, *J. Am. Chem. Soc.* **1971**, 93, 5189-5193

d) Furukawa, H.; Takeuchi, H.; Harada, I.; Tasumi, M. Matrix-isolation Infrared and Ultraviolet Spectroscopic Studies of Less Stable Conformers of 1,3,5-Hexatroene. *J Mol Struct,* **1983,** 100 341-350

Table S6 Experimental and calculated vibrational wavenumbers of 3-trans-1,3,5-Hexatriene in solid parahydrogen compared with those in Ar matrices.

Observed/parahydrogen [cm⁻¹]	Relative Intensity	Calculated [cm⁻¹] [a]	Relative Intensity [b]	Observed/ Ar matrix [cm⁻¹] [c]	Observed/ Ar matrix [cm⁻¹] [d]
		99.14	0.01		
		148.60	0.03		
		223.99	0.00		
		252.03	0.02		
		352.94	0.00	550 m	540 w
		444.78	0.00	600 w	
		544.57	0.08	660 w	
		613.10	0.00		682 w
		706.51	0.20	687 s	
		901.10	0.00		
900.9	1.00	926.30	1.00	900 vs	899 vs
		932.65	0.00		905 s
		946.12	0.00		938 w
		964.55	0.22	940 m	946 m
		978.67	0.04	950 sh	
				965 w	963 vw
		1019.36	0.00	990 w	
1012.02	0.38	1050.34	0.91	1015 vs	1012 vs
		1156.26	0.08		1016 sh
		1217.49	0.00	1135 sh	1137 vw
		1284.03	0.03	1143 m	
		1311.58	0.00	1260 w	1253 vw
		1324.08	0.05	1285 m	1281 vw
		1330.69	0.00	1305 m	1298 vw
		1433.75	0.00		1430 w
		1465.99	0.05	1440 m	
		1629.35	0.00	1460 w	
		1678.97	0.46	1612 m	
		1684.99	0.00		1628 m
				1640 m	
				1815 m	1804 m
				2990 w	2980 w,br
				3010 w	3014 m,br
				3025 m	
		3120.81	0.00		
		3121.01	0.00		
		3129.42	0.00		
		3133.87	0.32	3050 m	3043 m
		3135.24	0.00		3067 vw
		3136.66	0.43		3094 m
		3221.53	0.00		3101 sh
		3221.55	0.30	3110 m	

a) Vibrational wavenumbers of 3-cis-1,3,5-hexatriene were calculated with B3LYP/6-311+G(d,p) method.

b) Relative intensities were normalized to the most intense band of 926.3047 cm⁻¹ of 3-trans-1,3,5-hexatriene which was calculated to be 81.031 km/mol with B3LYP/6-311+G(d,p)

c) Datta, P.; Goldfarb , T.D.; Boikess, R.S. Photolysis of Matrix Isolated 1,3-Cyclohexadiene, cis-l,3,5-Hexatriene, and trans-l,3,5-Hexatriene, *J. Am. Chem. Soc.* **1971**, 93, 5189-5193

d) Furukawa, H.; Takeuchi, H.; Harada, I.; Tasumi, M. Matrix-isolation Infrared and Ultraviolet Spectroscopic Studies of Less Stable Conformers of 1,3,5-Hexatroene. *J Mol Struct,* **1983,** 100 341-350

Table S7. Calculated anharmonic vibrational wavenumbers (cm^{-1}) and relative intensities (listed in parentheses) of (E)- and (Z)-1,4,5-hexatrien-3ylium (HT) using B3LYP/6-311++G(2d,2p).

Mode[a]	E-HT		Z-HT	
ν_1 (A')	3099.5	(10.5)	3095.0	(14.1)
ν_2 (A')	3047.1	(11.9)	3037.7	(24.5)
ν_3 (A')	3006.3	(5)	3036.7	(3.2)
ν_4 (A')	3018.3	(14.4)	3053.3	(8.1)
ν_5 (A')	2989.4	(2.3)	3001.4	(4.4)
ν_6 (A')	2971.1	(22.3)	2960.7	(21.9)
ν_7 (A')	1890.1	(100)[b]	1882.2	(91.4)
ν_8 (A')	1530.9	(5.3)	1567.0	(3.8)
ν_9 (A')	1449.9	(3.8)	1444.9	(5.5)
ν_{10} (A')	1410.5	(1.1)	1414.6	(8)
ν_{11} (A')	1364.1	(3.2)	1350.9	(0)
ν_{12} (A')	1258.7	(1.4)	1336.7	(1.8)
ν_{13} (A')	1232.0	(5.5)	1270.9	(7.3)
ν_{14} (A')	1205.3	(2.1)	1163.6	(12.4)
ν_{15} (A')	1140.4	(0.1)	1111.6	(0.6)
ν_{16} (A')	1041.6	(3.3)	989.6	(4.5)
ν_{17} (A')	943.8	(2.7)	887.3	(0.6)
ν_{18} (A')	865.5	(68.1)	860.0	(84.5)
ν_{19} (A')	560.0	(24.6)	709.0	(31)
ν_{20} (A')	453.9	(1.2)	430.9	(3.1)
ν_{21} (A')	298.0	(2.9)	293.9	(4.8)
ν_{22} (A')	124.8	(0.2)	115.4	(0.1)
ν_{23} (A")	3020.8	(2.6)	3008.6	(3.5)
ν_{24} (A")	975.3	(52.5)	974.6	(33.6)
ν_{25} (A")	958.4	(0.2)	959.0	(0.5)
ν_{26} (A")	880.4	(25.6)	889.6	(10.8)
ν_{27} (A")	835.8	(52.4)	841.0	(100)[b]
ν_{28} (A")	805.5	(6.7)	765.0	(10.3)
ν_{29} (A")	575.0	(10.8)	586.6	(20.1)
ν_{30} (A")	534.7	(0.1)	526.4	(0.1)
ν_{31} (A")	307.7	(5.1)	288.1	(14.5)
ν_{32} (A")	208.4	(0)	209.8	(0)
ν_{33} (A")	119.6	(2.2)	113.8	(1.9)

[a] The optimized structures of (E)- and (Z)-1,4,5-hexatrien-3ylium belong to the point group of Cs symmetry.

[b] Relative intensities listed in parentheses were normalized to the most intense E-HT band at 1890.1 cm^{-1} and Z-HT band at 841.0 cm^{-1}, which were calculated to be 74.532 km/mol (E-HT) and 58.281 km/mol (Z-HT), respectively.

Table S8. Calculated anharmonic vibrational wavenumbers (cm^{-1}) and relative intensities (listed in parentheses) of α-hydrogenated fulvene (α-HF) and β-hydrogenated fulvene (β-HF) using B3LYP/6-311++G(2d,2p).

Mode[a]	a-HF		b-HF	
ν_1 (A')	3100.3	(12.9)	3109.6	(10.7)
ν_2 (A')	3098.1	(10.8)	3063.4	(8.4)
ν_3 (A')	3082.3	(16.1)	3090.5	(17.6)
ν_4 (A')	3067.0	(8.2)	3082.4	(5.1)
ν_5 (A')	3071.7	(10.4)	3069.0	(11.2)
ν_6 (A')	2903.0	(14.1)	2871.4	(39.3)
ν_7 (A')	1554.5	(11.4)	1569.5	(0.9)
ν_8 (A')	1472.9	(0.4)	1456.4	(9.4)
ν_9 (A')	1391.5	(21.2)	1411.8	(1.4)
ν_{10} (A')	1384.3	(0.1)	1385.6	(13)
ν_{11} (A')	1366.4	(5.3)	1344.1	(15.4)
ν_{12} (A')	1285.9	(2.3)	1294.7	(2.6)
ν_{13} (A')	1246.2	(1.4)	1238.4	(3.7)
ν_{14} (A')	1227.9	(4)	1226.5	(1.9)
ν_{15} (A')	1088.1	(7.9)	1090.7	(0.9)
ν_{16} (A')	1027.4	(3.1)	1001.0	(4.3)
ν_{17} (A')	970.0	(6.7)	941.1	(7.6)
ν_{18} (A')	931.9	(15)	934.5	(10.1)
ν_{19} (A')	849.1	(1.2)	905.2	(6)
ν_{20} (A')	807.4	(5.4)	781.2	(2.9)
ν_{21} (A')	632.7	(2.3)	648.6	(1.2)
ν_{22} (A')	348.8	(0.1)	348.1	(1.1)
ν_{23} (A")	2909.9	(6.9)	2866.2	(13.6)
ν_{24} (A")	1112.6	(0.9)	1093.1	(1.4)
ν_{25} (A")	929.6	(5.2)	944.3	(0.3)
ν_{26} (A")	896.0	(1.4)	891.0	(27.7)
ν_{27} (A")	806.0	(100)[b]	754.0	(100)[b]
ν_{28} (A")	770.4	(0.6)	740.9	(4.3)
ν_{29} (A")	661.0	(68.5)	649.2	(0.1)
ν_{30} (A")	597.3	(4.5)	577.6	(66)
ν_{31} (A")	516.4	(11.1)	524.1	(2.7)
ν_{32} (A")	387.0	(23.6)	355.9	(0.5)
ν_{33} (A")	180.3	(0)	217.6	(8.1)

[a] The optimized structures of a-hydrogenated fulvene (a-HF) and b-hydorogenated fulvene (b-HF) belong to the point group of Cs symmetry.
[b] Relative intensities listed in parentheses were normalized to the most intense α-HF band at 806.0 cm^{-1} and β-HF band at 754.0 cm^{-1}, which were calculated to be 61.8121 km/mol (α-HF) and 62.2103 km/mol (β-HF), respectively.

Table S9. Experimental and calculated vibrational wavenumbers of 1,3-Hexatriene-5-yne in solid parahydrogen compared with those in vapor phase.

cis-1,3-Hexatriene-5-yne				trans-1,3-Hexatriene-5-yne				Vapor/ [cm^{-1}] [d]
Observed/ para-H$_2$ [cm^{-1}]	Relative Intensity	Calculated [cm^{-1}] [a]	Relative intensity [b]	Observed / para-H$_2$ [cm^{-1}]	Relative Intensity	Calculated [cm^{-1}] [a]	Relative Intensity [c]	
		127.027	0.001			134.323	0.011	
		138.000	0.007			139.709	0.018	
		269.215	0.013			206.788	0.006	
		306.923	0.106			308.942	0.037	
		428.996	0.017			449.333	0.009	
		472.150	0.205			460.634	0.002	
630.43	0.87	641.661	0.611			556.095	0.070	
		685.770	0.517	624.58	0.76	636.946	0.515	
		690.200	0.112			666.104	0.108	
		716.337	0.043			687.437	0.497	781
		807.072	0.123			881.396	0.085	845
								908
		894.267	0.009	914.34	0.71	939.362	0.308	913
923.25	0.38	943.478	0.591			959.590	0.009	942
		986.047	0.000			974.332	0.229	
		986.973	0.105			1035.047	0.066	
		1040.549	0.189	1014	0.23	1040.104	0.475	1000
		1166.593	0.002			1193.431	0.019	
		1265.089	0.006			1286.439	0.003	1210
		1317.851	0.027			1313.521	0.008	1246
		1394.677	0.006			1331.289	0.044	1286
		1466.924	0.078			1451.883	0.024	1434
		1620.545	0.075			1637.510	0.069	1575
		1679.462	0.010			1681.529	0.035	1610
								1736
								1822
		2187.038	0.082			2189.323	0.092	2090
		3132.698	0.062			3130.247	0.014	
		3141.970	0.004			3131.307	0.121	
		3154.378	0.010			3138.090	0.029	
		3162.162	0.165			3153.566	0.135	3065
		3222.744	0.112			3224.790	0.096	3122
3326.9	1	3476.186	1.000	3324.70	0.56			
3327.3	0.61			3325.30	1	3475.888	1.000	3346

a) Vibrational wavenumbers of 1,3,5-hexadiene-5-yne (cis and trans) were calculated with B3LYP/6-311+G(d,p) method.

b) Relative intensities were normalized to the most intense band of 3476.186 cm^{-1} of 1,3-hexadiene-5-yne (cis) which was calculated to be 90.0555 km/mol with B3LYP/6-311+G(d,p)

c) Relative intensities were normalized to the most intense band of 3475.888 cm^{-1} of 1,3-hexadiene-5-yne (trans) which was calculated to be 101.757 km/mol with B3LYP/6-311+G(d,p)

d) Georgieff, K.K.; Cave, W.T.; Blaikie, K.G. Acetylene Polymers: Preparation, Physical Properties, Infrared and Ultraviolet. Spectra, *J. Am. Chem. Soc.,* **1954**, 76, 5494-5499

Table S10. Experimental and calculated vibrational wavenumbers of *o*-benzyne in solid parahydrogen compared with those in other matrices.

Observed/ parahydrogen [cm⁻¹]	Relative Intensity	Calculated [cm⁻¹][a]	Relative Intensity [b]	Sym. in C_{2v}	Observed/ Ar matrix [c] [cm⁻¹]	Observed/ N₂ matrix [d] [cm⁻¹]	Observed/ N₂ matrix [e] [cm⁻¹]	Observed /Ar matrix [f] [cm⁻¹]	Relative Intensity
		393.848	0.058	b₁	469	472	470	388	(0.05)
		421.867	1.000	b₂				472	(1.00)
		624.304	0.003	a₁				589	(0.00)
735	1	749.402	0.791	b₁	736	743	739	737	(0.59)
								838	(0.00)
844	0.6	845.072	0.283	b₂	849	847	848	849	(0.31)
		925.066	0.000	b₁					
		997.386	0.071	a₁				982	(0.06)
					1038	1039	1038	1039	(0.13)
1057	0.26	1073.133	0.217	a₁	1053	1056	1055	1055	(0.09)
		1107.516	0.017	b₂				1094	(0.02)
		1161.698	0.000	a₁					
		1270.218	0.001	b₂				1271	(0.02)
		1304.825	0.013	a₁				1307	(0.00)
							1355		
		1422.118	0.020	b₂			1395	1394	(0.07)
								1415	(0.00)
		1464.201	0.128	b₂	1451	1448	1448	1451	(0.11)
		1480.034	0.009	a₁					
					1607	1598	1596		
		2008.468	0.002	a₁				1846	(0.02)
						2084	2082		
		3160.205	0.009	b₂				3049	(0.01)
		3175.532	0.034	a₁				3071	(0.01)
		3198.587	0.216	b₂		3088		3086	(0.11)
		3201.938	0.059	a₁				3094	(0.07)

[a] Vibrational wavenumbers of *o*-benzyne were calculated with B3LYP/6-311+G(d,p) method.

[b] Relative intensities were normalized to the most intense band of 421.867 cm⁻¹ of *o*-benzyne, which was calculated to be 113.61 km/mol with B3LYP/6-311+G(d,p)

[c] Chapman, O.L.; Mattes, K.; McIntosh, C.L.; Pancansky, J.; Calder, G.V.; Orr, G. Photochemical Transformations. LII. Benzyne. *J. Am. Chem. Soc.* **1973,** 95, 6134-6135

[d] Dunkin I.R.; MacDonald, J.G. Matrix photolysis of unsaturated cyclic anhydrides and the infrared spectrum of tetradeuteriobenzyne. *J. Chem. Soc.,Chem. Comm.* **1979,** 772-773

[e] Nam, H.H.; Leroi, G.E. On the vibrational spectrum of matrix isolated *o*-benzyne. *J. Mol. Struct.* **1987**, 157, 301-304

[f] Radziszewski, J. G.; Hess, B. A.; Zahradnik, R. Infrared Spectrum of *o*-Benzyne: Experiment and Theory. *J Am Chem Soc* **1992**, *114*, 52–57.   Values in parentheses are reported intensities.