Supporting Information

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A. Geometries

A.1 The cartesian coordinates from the archives of the optimized geometries of the ***σ radicals*** *of phenylethynyl*

(i) B3LYP/DZP++


```
1\1\GINC-NODE18\FOpt\UB3LYP\Gen\C8H5(2)\I_RAJKS\09-Sep-2006\4\\# B3LYP
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(ii) MP2/DZP++


```
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```


A.2 The imaginary frequency in the C_{2v} geometry of phenylethynyl radical

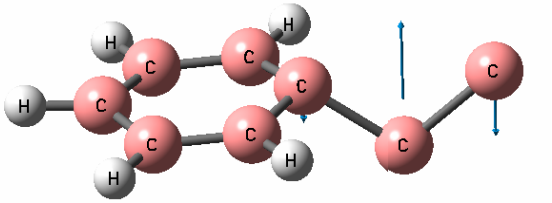


Figure 1. The imaginary frequency (597*i* cm^{-1}) in phenylethynyl radical. The π radical is a transition state at the C_{2v} geometry with the BLYP/DZP++ level of theory.

B. IR frequencies of phenylethynyl

Table 1. The IR vibrational frequencies (cm^{-1}) of phenylethynyl radical predicted by the MP2/cc-pVDZ and MP2/DZP++ methods.

MP2/cc-pVDZ		**MP2/DZP++**	
Radical	*Anion*	*Radical*	*Anion*
Freq	Freq	Freq	Freq
168	139	143	81
182	144	152	119
433	326	420	132
480	405	425	276
496	466	494	377
569	485	497	415
621	518	622	464
667	619	649	467
793	620	672	623
809	728	824	683
886	761	831	762
1022	832	952	766
1026	860	1013	771
1107	919	1052	839
1114	930	1060	843
1114	1003	1077	1006
1163	1043	1095	1042
1164	1076	1155	1084
1177	1152	1178	1164
1221	1173	1200	1188
1250	1207	1265	1205
1256	1298	1288	1319
1364	1418	1370	1424
1582	1491	1549	1490
1626	1499	1565	1502
1882	1600	1763	1603
1895	1643	1781	1644
2518	1988	2344	1970
3239	3175	3263	3194
3251	3183	3276	3202
3262	3208	3283	3226
3271	3216	3292	3234
3271	3221	3294	3239

Table 2. The IR vibrational frequencies (cm^{-1}) of phenylethyne predicted by the B3LYP/DZP++ and MP2/DZP++ methods.

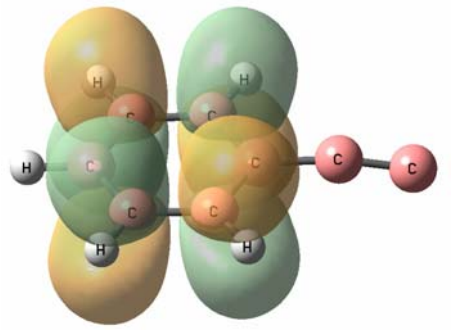
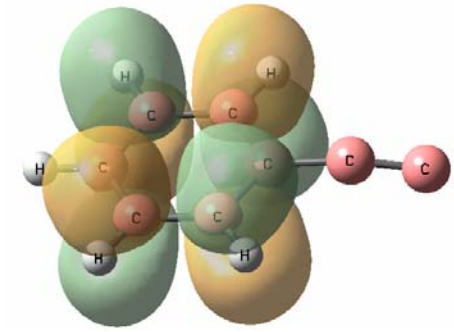
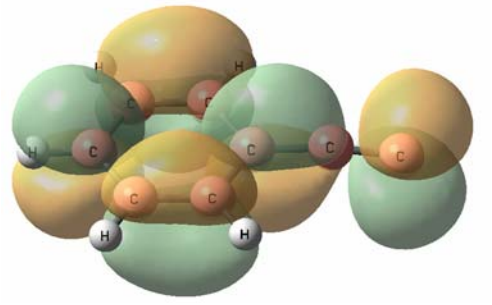
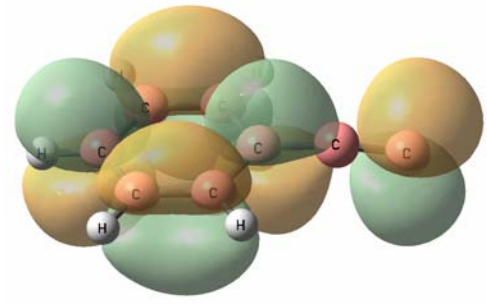
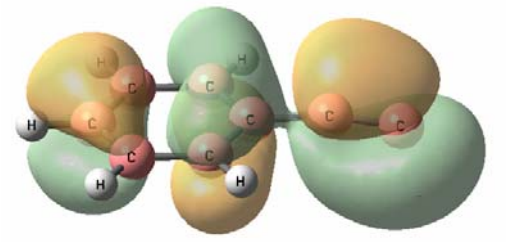
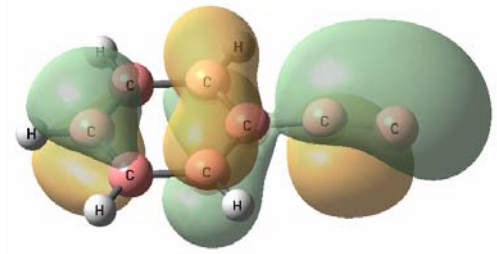
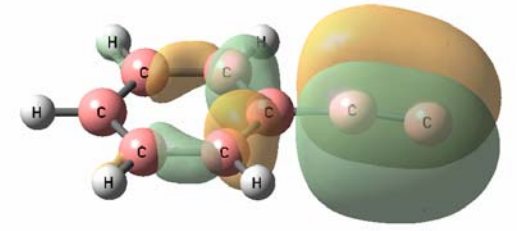
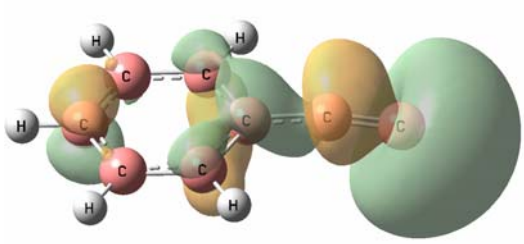
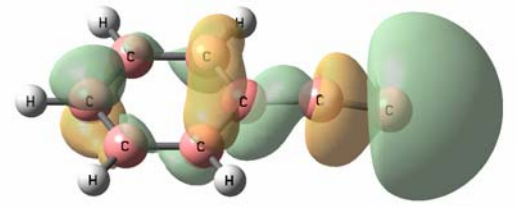
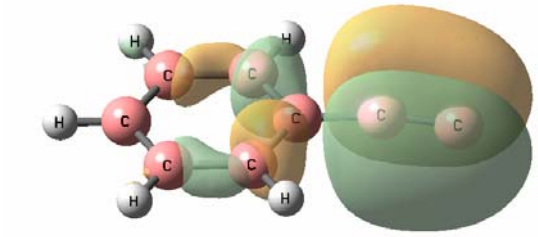
B3LYP/DZP++		**MP2/DZP++**	
Radical	*Radical anion*	*Radical*	*Radical anion*
Freq	Freq	Freq	Freq
150	134	138	120
152	152	139	151
379	289	311	219
414	431	381	266
466	454	424	410
514	472	462	444
555	515	466	453
611	606	494	464
626	617	570	505
647	619	621	576
706	650	626	637
769	673	710	657
786	747	770	742
869	783	810	761
944	792	843	781
996	931	870	936
1004	944	876	940
1014	976	1012	977
1043	992	1049	979
1097	1073	1103	993
1175	1131	1182	1162
1193	1177	1204	1202
1218	1233	1228	1304
1322	1274	1339	1325
1354	1352	1451	1346
1465	1419	1487	1419
1512	1464	1521	1467
1613	1497	1629	1599
1644	1618	1658	1885
2185	1966	2113	2299
3181	3122	3232	3179
3189	3125	3239	3180
3200	3132	3249	3219
3207	3165	3255	3223
3213	3166	3263	3248
3466	3178	3497	3525

Table 3. Harmonic vibrational frequencies (cm^{-1}), IR intensities (km/mol), and mode assignments of the phenylethynyl radical and anion predicted with the B3LYP/DZP++ method.

Radical					**Anion**			
Vibrational mode	Symmetry	Frequency	IR intensity	Mode assignment	Symmetry	Frequency	IR intensity	Mode assignment
ω_1	B_1	58	41	Ethynyl bending out the C_s plane	B_1	145	9	Molecule bending out the C_s plane
ω_2	B_2	138	3	Ethynyl bending in the C_s plane	B_2	146	6	C–C≡C bending in the C_s plane
ω_3	B_1	200	15	CCC wagging in ring	B_1	340	0.3	C–C≡C bending out of plane
ω_4	A_2	389	0	Ring distortion	A_2	423	0	Ring distortion
ω_5	A_1	467	1.7	CCC bending in the ring	A_1	469	5	CCC bending in ring
ω_6	B_1	472	13	CCC bending in the ring	B_2	484	5	C–C≡C bending in plane
ω_7	B_2	481	2	Ethynyl bending in C_s plane	B_1	539	6	C–C–C wagging out of plane
ω_8	B_2	614	0.2	Ring distortion	B_2	624	0.1	Distortion in ring by CCC scissoring
ω_9	B_1	683	37	C-H wagging in the ring	B_1	704	31	Distortion in ring out of plane
ω_{10}	A_1	771	0.5	CCC bending in the ring	A_1	764	11	C-H wagging in the ring
ω_{11}	B_1	789	34	C-H wagging in phase	B_1	766	57	CCC bending in the ring
ω_{12}	A_2	861	0	C-H wagging out of phase	A_2	849	0	C-H wagging out of phase
ω_{13}	B_1	963	1.1	C-H wagging out of phase	B_1	898	11	C-H wagging in plane
ω_{14}	A_1	996	3	CCC bending in the ring	A_2	975	0	C-H wagging out of plane
ω_{15}	A_2	1005	0	C-H wagging	B_1	975	0.3	C-H wagging out of plane
ω_{16}	B_1	1021	0.5	C-H wagging	A_1	992	26	CCC scissoring in the ring
ω_{17}	A_1	1032	0.3	CC anti-symmetric stretching in the ring	A_1	1035	14	CC stretching in the ring
ω_{18}	B_2	1098	6	CC symmetric stretch in the ring	B_2	1079	8	CC symmetric stretching in the ring
ω_{19}	A_1	1172	54	C-C≡ stretch	B_2	1156	1.0	CH wagging in plane
ω_{20}	B_2	1175	1.7	CH wagging in plane	A_1	1178	32	CC stretching in the ring
ω_{21}	A_1	1211	17	CH wagging in plane	A_1	1207	67	CCC bending in the ring
ω_{22}	B_2	1315	1.2	CC anti-symmetric stretching in the ring	B_2	1298	0	CC anti-symmetric stretching in the ring
ω_{23}	B_2	1359	11	CC anti-symmetric stretching in the ring	B_2	1345	2	CC anti-symmetric stretching in the ring
ω_{24}	B_2	1456	12	CC symmetric stretching in the ring	B_2	1456	0.7	CC anti-symmetric stretching in the ring (in phase)
ω_{25}	A_1	1485	0.1	CC anti-symmetric stretching in the ring	A_1	1493	54	CC symmetric stretching (in phase)
ω_{26}	B_2	1576	0.6	CC anti-symmetric stretching in the ring	B_2	1579	6	CC anti-symmetric stretching (out of phase)
ω_{27}	A_1	1612	79	CC stretching in the ring	A_1	1626	190	CC symmetric stretching in phase
ω_{28}	A_1	**1966**	86	Ethynyl stretching	A_1	**2032**	444	Ethynyl C≡C symmetric stretch
ω_{29}	A_1	3189	0.1	CH stretch	A_1	3137	13	CH stretch
ω_{30}	B_2	3199	5	CH stretch	B_2	3144	50	CH stretch
ω_{31}	A_1	3208	10	CH stretch	A_1	3172	72	CH stretch
ω_{32}	B_2	3219	5	CH stretch	B_2	3186	51	CH stretch
ω_{33}	A_1	3222	5	CH stretch	A_1	3191	3	CH stretch

Table 4. Harmonic vibrational frequencies (cm^{-1}) of the *o-, m-* and *p*-ethynylphenyl radicals and anions optimized with the B3LYP/DZP++ method. The IR intensities (km/mol) are given in parentheses.

Vibrational modes	***ortho***		***meta***		***para***	
	radical	*anion*	*radical*	*anion*	*radical*	*anion*
	Frequencies	Frequencies	Frequencies	Frequencies	Frequencies	Frequencies
ω_1	147 (3)	138 (5)	147 (1)	145 (0)	153 (1)	149 (7)
ω_2	150 (2)	165 (6)	152 (1)	156 (3)	156 (0)	159 (0)
ω_3	376 (3)	351 (5)	370 (3)	333 (2)	388 (12)	356 (0)
ω_4	418 (2)	396 (8)	419 (2)	392 (8)	401 (0)	379 (18)
ω_5	458 (1)	460 (5)	459 (0)	461 (2)	469 (2)	445 (100)
ω_6	496 (1)	480 (84)	515 (4)	481 (82)	512 (3)	458 (7)
ω_7	548 (2)	530 (12)	554 (0)	521 (0)	528 (9)	522 (2)
ω_8	616 (55)	560 (57)	616 (62)	558 (3)	608 (3)	553 (1)
ω_9	620 (3)	575 (0)	617 (0)	576 (69)	609 (56)	598 (63)
ω_{10}	649 (49)	612 (1)	647 (53)	612 (1)	651 (50)	639 (0)
ω_{11}	686 (0)	695 (13)	673 (19)	713 (16)	689 (2)	695 (2)
ω_{12}	763 (5)	759 (2)	758 (1)	758 (1)	750 (7)	748 (4)
ω_{13}	764 (74)	769 (38)	784 (44)	776 (27)	817 (65)	811 (20)
ω_{14}	866 (2)	870 (0)	877 (11)	873 (0)	822 (0)	857 (0)
ω_{15}	958 (2)	929 (0)	915 (4)	925 (2)	957 (1)	955 (2)
ω_{16}	976 (1)	955 (3)	987 (1)	966 (0)	973 (0)	960 (1)
ω_{17}	996 (0)	976 (0)	989 (0)	989 (2)	982 (0)	969 (0)
ω_{18}	1036 (6)	1032 (5)	1050 (7)	1005 (2)	1042 (9)	1027 (6)
ω_{19}	1115 (5)	1087 (7)	1085 (8)	1096 (4)	1103 (5)	1079 (1)
ω_{20}	1166 (0)	1148 (0)	1171 (0)	1171 (5)	1172 (0)	1181 (16)
ω_{21}	1215 (2)	1172 (2)	1196 (1)	1186 (7)	1208 (2)	1221 (0)
ω_{22}	1245 (1)	1240 (4)	1285 (0)	1274 (32)	1292 (0)	1269 (10)
ω_{23}	1334 (0)	1276 (54)	1311 (1)	1322 (10)	1330 (1)	1312 (2)
ω_{24}	1430 (4)	1402 (13)	1429 (4)	1359 (0)	1379 (4)	1389 (1)
ω_{25}	1465 (14)	1421 (1)	1472 (17)	1440 (0)	1468 (14)	1444 (5)
ω_{26}	1566 (0)	1556 (2)	1545 (5)	1525 (3)	1592 (1)	1524 (7)
ω_{27}	1632 (0)	1578 (8)	1633 (9)	1578 (22)	1604 (0)	1573 (71)
ω_{28}	**2191** (6)	2130 (198)	**2183** (5)	2131 (299)	**2186** (10)	2136 (338)
ω_{29}	3179 (0)	3040 (90)	3181 (6)	3038 (89)	3187 (3)	3044 (15)
ω_{30}	3190 (3)	3088 (169)	3199 (7)	3073 (67)	3188 (0)	3044 (181)
ω_{31}	3197 (12)	3112 (79)	3202 (0)	3093 (181)	3202 (12)	3114 (182)
ω_{32}	3208 (12)	3151 (103)	3212 (6)	3163 (48)	3205 (0)	3116 (39)
ω_{33}	3466 (97)	3471 (72)	3465 (98)	3472 (97)	3466 (97)	3473 (110)

	Alpha orbitals		Beta orbitals	
LUAO+1		A"	LUBO+2	 A"
LUAO		A'	LUBO+1	 A'
HOAO = SOMO		A'	LUBO	 A'
HOAO-1		A"	HOBO	 A'
HOAO-2		A'	HOBO-1	 A"

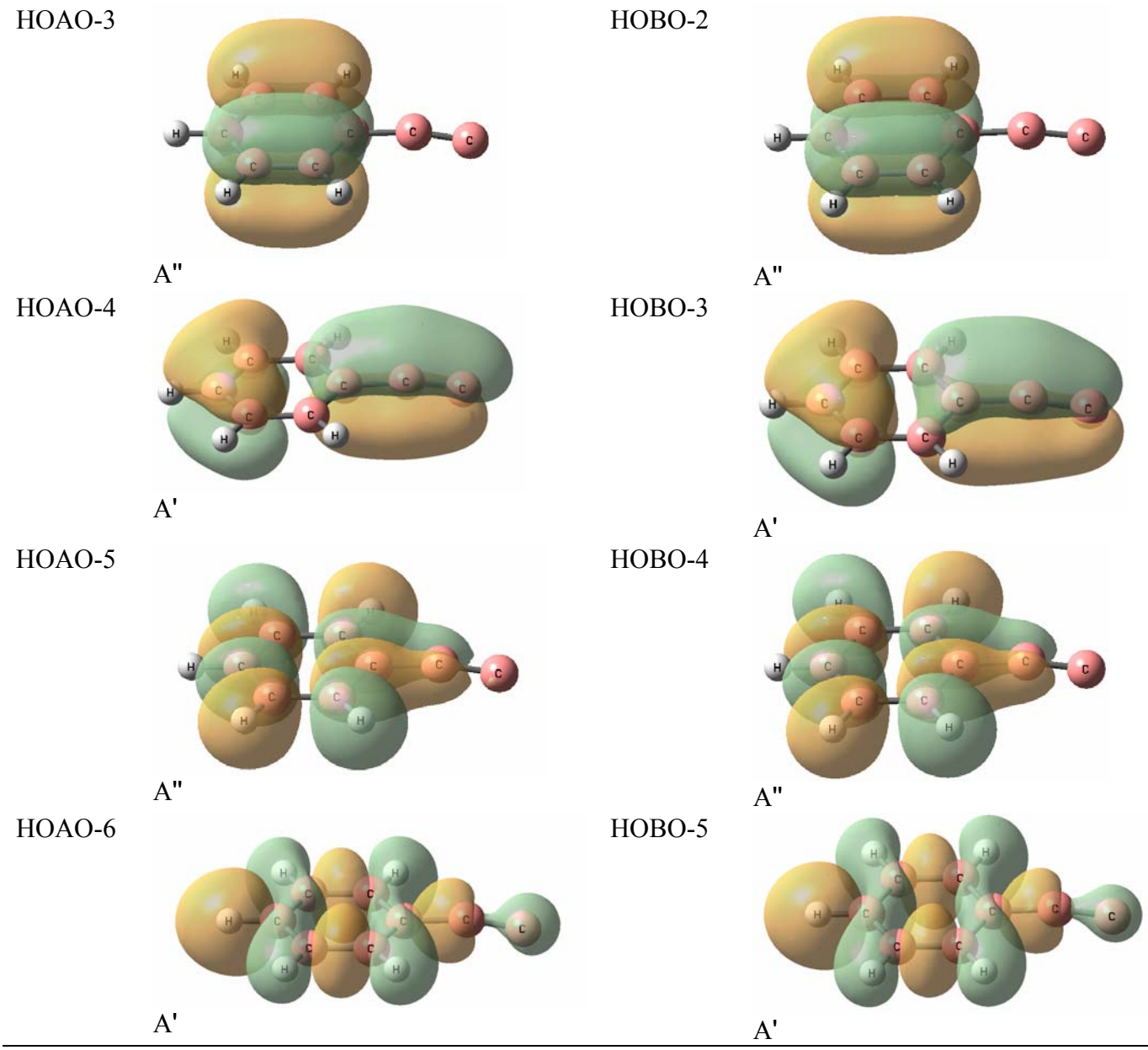


Figure 2. Qualitative molecular orbital diagrams of the C_s phenylethynyl radical (**equilibrium geometry**) optimized with the BLYP/DZP++ basis set. HOAO is the highest occupied alpha orbital and HOBO is the highest beta orbital. LUAO is the lowest unoccupied alpha orbital and LUBO is the lowest unoccupied beta orbital.

D. π - σ Energy separation in the isomers of phenylethynyl

Table 5. The π and σ radicals energy separations in the *o*-, *m*-, and *p*-ethynylphenyl.

	Methods	E(π radical)		E(σ radical)		$\Delta E_{\sigma-\pi}$	
			E_{elec}		E_{elec}		
			Hartrees		*Hartrees*	*Hartrees*	kcal/mol
ortho	B3LYP/DZP++	C_s ($^2A'$)	-307.73933	C_s ($^2A''$)	-307.66542	-0.073904	-46.4
	MP2/DZP++	C_s ($^2A'$)	-306.71633	C_s ($^2A''$)	-306.64077	-0.075555	-47.4
meta	B3LYP/DZP++	C_s ($^2A'$)	-307.74093	C_s ($^2A''$)	-307.65834	-0.082582	-51.8
	MP2/DZP++	C_s ($^2A'$)	-306.71851	C_s ($^2A''$)	-306.63843	-0.080080	-50.3
para	B3LYP/DZP++	C_{2v} ($^2A_1$)	-307.74059	C_{2v} ($^2B_1$)	-307.66465	-0.075941	-47.7
	MP2/DZP++	C_{2v} ($^2A_1$)	-306.70022	C_{2v} ($^2B_1$)	-306.77698	-0.076812	-48.2