Supplementary Material (ESI) for *Physical Chemistry Chemical Physics*

Supplementary Information

Theoretical study of multiphoton ionization of cyclohexadienes and unimolecular decomposition of their mono- and dications

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Table S1. Single and double ionization potentials (IP) of 1,3-cyclohexadiene (1,3-CHD) and 1,4-cyclohexadiene (1,4-CHD).[a] The resonant wavelength λ is 800nm = 1.55 eV = 35.7 kcal/mol.

molecule	MO	IP, eV	IP/λ	molecule	MO	IP, eV	IP/λ	method
1,3-CHD→				1,4-CHD→				
1,3-CHD^{+} [b]	HOMO	7.86	5.1	1,4-CHD^{+} [c]	HOMO	8.36	5.4	B3LYP/6-31G**
		8.22	5.3			8.85	5.7	CCSD(T)/cc-pvdz//B3LYP/6-31G**
		8.20	5.3			8.79	5.7	OVGF/6-311+G*
		8.25	5.3					Expt.[10]
	HOMO-1	10.90	7.0		HOMO-1	9.69	6.3	OVGF/6-311+G*
	HOMO-2	11.19	7.2		HOMO-2	11.02	7.1	OVGF/6-311+G*
	HOMO-3	11.70	7.6		HOMO-3	12.18	7.9	OVGF/6-311+G*
	HOMO-4	12.76	8.2		HOMO-4	13.14	8.5	OVGF/6-311+G*
1,3-CHD^{2+} [d]	HOMO	22.58	14.6	1,4-CHD^{2+} [e]	HOMO	23.19	15.0	B3LYP/6-31G**
		22.81	14.7			23.40	15.1	CCSD(T)/cc-pvdz// B3LYP/6-31G**
		22.86	14.8			23.19	15.0	OVGF/6-311+G*
		23.1	14.9					Expt.[10,23]
	HOMO-1	25.11	16,2		HOMO-1	23,83	15,4	OVGF/6-311+G*

	HOMO-2	25.20	16,3		HOMO-2	25,50	16,5	OVGF/6-311+G*
	HOMO-3	25.80	16,6		HOMO-3	26,83	17,3	OVGF/6-311+G*
	HOMO-4	26.61	17,2		HOMO-4	27,40	17,7	OVGF/6-311+G*
	HOMO-5	27.29	17,6		HOMO-5	28,56	18,4	OVGF/6-311+G*
	HOMO-6	28.46	18,4		HOMO-6	28,37	18,3	OVGF/6-311+G*
	HOMO-7	28.61	18,5					OVGF/6-311+G*
	HOMO-8	28.73	18.5					OVGF/6-311+G*
		29.1	18.8					Expt.[10,23]
	HOMO-9	30.33	19.6					OVGF/6-311+G*
1,3-CHD^{2+} [f]	HOMO	24.17	15.6	1,4-CHD^{++} [g]	HOMO	23.10	14.9	B3LYP/6-31G**
		24.59	15.9			23.52	15.2	CCSD(T)/cc-pvdz// B3LYP/6-31G**

[a]For 1,3- and 1,4- cyclohexadiene singlet isomer is more stable then triplet one on 2.34 and 4.27 eV, respectively, according to the CCSD(T)/cc-pvdz//B3LYP/6-31G** calculation.

[b]Computed at the geometry of the neutral singlet 1,3-CHD isomer.

[c]Computed at the geometry of the neutral singlet 1,4-CHD isomer.

[d]Dication in singlet electronic state computed at the geometry of the neutral singlet 1,3-CHD isomer.

[e]Dication in singlet electronic state computed at the geometry of the neutral singlet 1,4-CHD isomer.

[f]Dication in triplet electronic state computed at the geometry of the neutral singlet 1,3-CHD isomer.

[g]Dication in triplet electronic state computed at the geometry of the neutral singlet 1,4-CHD isomer.

Table S2. Single ionization potentials (IP) for the 1,3-cyclohexadiene (1,3-CHD^{+}) and 1,4-cyclohexadiene (1,4-CHD^{+}) monocations.

The resonant wavelength λ is 800nm = 1.55 eV = 35.7 kcal/mol.

molecule	MO	IP, eV	IP/λ	molecule	MO	IP, eV	IP/λ	method
1,3-CHD^{+}→				1,4-CHD→				
1,3-CHD^{++} singlet[a]	HOMO	14.15	9.13	1,4-CHD^{++} singlet[b]	HOMO	14.46	9.33	B3LYP/6-31G**
	HOMO	14.04	9.06		HOMO	14.26	9.20	CCSD(T)/cc-pvdz//B3LYP/6-31G**
	HOMO	14.67	9.46		HOMO	14.40	9.30	OVGF/6-311+G*
1,3-CHD^{++} triplet[a]	HOMO	16.27	10.50	1,4-CHD^{++} triplet[b]	HOMO	14.60	9.42	B3LYP/6-31G**
	HOMO	16.33	10.53		HOMO	14.57	9.40	CCSD(T)/cc-pvdz//B3LYP/6-31G**

[a]Computed at the geometry of monocation 1,3-CHD^{+}.

[b]Computed at the geometry of monocation 1,4-CHD^{+}.

Table S3. Excitation energies (E_e, in eV) and oscillator strengths (*f*) for 1,3-CHD^+ and 1,4-CHD^+ calculated at various levels of theory (λ = 1.55 eV).

Transition	E_e, 1,3-CHD^+	*f*	E_e/λ	E_e, 1,4-CHD^+	*f*	E_e/λ	Method
(HOMO-1→HOMO)	2.73	0.0659	-	0.62	0.0467	-	CASSCF(13,12)/6-311+G*
	2.55	-	-	0.75	-	-	CASPT2(13,12)/6-311+G*
	2.72	-	-	0.90	-	-	UOVGF/6-311+G*
	3.13	-	-	-	-	-	CIS/aug-cc-pvdz
	3.14	0.1124		1.02	0.0084	0.66	CISD/aug-cc-pvdz
	2.81	0.0358	1.81	1.17	0.0314	0.75	TD(B3LYP)/aug-cc-pvdz
(HOMO-1→LUMO)	5.92			6.68			CIS/aug-cc-pvdz
	5.85	0.0698		7.67	0.0000		CISD/aug-cc-pvdz
	5.82	0.0023	3.75				TD(B3LYP)/aug-cc-pvdz
	4.97	0.0646					CASSCF(13,12)/6-311+G*
	5.44						CASPT2(13,12)/6-311+G*
(HOMO-1→LUMO, HOMO→LUMO+1)				6.54	0.0248	4.22	TD(B3LYP)/aug-cc-pvdz
(HOMO→LUMO+1, HOMO-1→LUMO)				4.63	0.0194	2.99	TD(B3LYP)/aug-cc-pvdz
				3.97	0.0106		CASSCF(13,12)/6-311+G*
				4.61			CASPT2(13,12)/6-311+G*
(HOMO-1→LUMO+1)	8.81	-	-	-			CIS/aug-cc-pvdz
	7.75	0.4341	5.00	-			CISD/aug-cc-pvdz
	-	-	-	6.42	0.0000		TD(B3LYP)/aug-cc-pvdz
(HOMO-1→LUMO+2)				7.92			CIS/aug-cc-pvdz
				8.86	0.0292	5.72	CISD/aug-cc-pvdz
(HOMO-1→LUMO+3)				7.90			CIS/aug-cc-pvdz
				8.93	0.0273	5.76	CISD/aug-cc-pvdz
(HOMO-2→LUMO+1)				8.07			CIS/aug-cc-pvdz

				7.53	0.0005		CISD/aug-cc-pvdz
(HOMO-1→LUMO+5)				4.30			CIS/aug-cc-pvdz
				5.09	0.0095		CISD/aug-cc-pvdz
				4.09	0.0000		TD(B3LYP)/aug-cc-pvdz
(HOMO-2→HOMO)	3.00			2.23			UOVGF/6-311+G*
	4.64			3.11	0.0000		CIS/aug-cc-pvdz
	3.33	0.0003		2.21	0.0000		CISD/aug-cc-pvdz
	2.75	0.0009		2.10	0.0000		TD(B3LYP)/aug-cc-pvdz
				2.58	0.0000		CASSCF(13,12)/6-311+G*
				2.70			CASPT2(13,12)/6-311+G*
(HOMO-3→HOMO)	5.12			4.30			CIS/aug-cc-pvdz
	3.71	0.0013		3.30	0.0060		CISD/aug-cc-pvdz
	3.19	0.0005		3.22	0.0033		TD(B3LYP)/aug-cc-pvdz
	3.71	0.0009					CASSCF(13,12)/6-311+G*
	4.00						CASPT2(13,12)/6-311+G*
(HOMO-4→HOMO)	7.21			6.22			CIS/aug-cc-pvdz
	5.41	0.0034	3.49	5.26	0.0240	3.40	CISD/aug-cc-pvdz
	4.18	0.0293	2.70	4.95	0.0372	3.19	TD(B3LYP)/aug-cc-pvdz
	4.27	0.1879		5.10	0.0093		CASSCF(13,12)/6-311+G*
	4.63			5.15			CASPT2(13,12)/6-311+G*
(HOMO-4→HOMO,	6.78						CIS/aug-cc-pvdz
HOMO-8→HOMO)	6.10	0.0010					CISD/aug-cc-pvdz
(HOMO-5→HOMO)	7.48			5.40			CIS/aug-cc-pvdz
	5.50	0.0079	3.55	4.35	0.0000		CISD/aug-cc-pvdz
	4.70	0.0000		4.09	0.0000		TD(B3LYP)/aug-cc-pvdz
(HOMO-6→HOMO)	6.74			7.02			CIS/aug-cc-pvdz
	5.33	0.0058	3.44	6.06	0.0000		CISD/aug-cc-pvdz
	5.40	0.0000		4.74	0.0000		TD(B3LYP)/aug-cc-pvdz
				4.60	0.0000		CASSCF(13,12)/6-311+G*
				4.63			CASPT2(13,12)/6-311+G*

(HOMO-7→HOMO)	8.99			5.76			CIS/aug-cc-pvdz
	7.93	0.0046		5.04	0.0000		CISD/aug-cc-pvdz
	6.09	0.0098	3.94	5.69	0.0000		TD(B3LYP)/aug-cc-pvdz
(HOMO-8→HOMO)				6.50	0.0000		TD(B3LYP)/aug-cc-pvdz
(HOMO-9→HOMO)	5.69	0.0012					TD(B3LYP)/aug-cc-pvdz
(HOMO-10→HOMO)				7.30	0.0008		TD(B3LYP)/aug-cc-pvdz
(HOMO-2→LUMO)	7.45						CIS/aug-cc-pvdz
	6.41	0.0026					CISD/aug-cc-pvdz
	6.60	0.0016		6.76	0.0002		TD(B3LYP)/aug-cc-pvdz
(HOMO-3→LUMO)	7.75						CIS/aug-cc-pvdz
	6.78	0.0000					CISD/aug-cc-pvdz
	6.21	0.0012					TD(B3LYP)/aug-cc-pvdz
(HOMO-4→LUMO,	9.20						CIS/aug-cc-pvdz
HOMO-5→LUMO,	7.61	0.0024					CISD/aug-cc-pvdz
HOMO-7→HOMO)							
(HOMO-8→HOMO)				7.03			CIS/aug-cc-pvdz
				5.95	0.0000		CISD/aug-cc-pvdz
				5.55	0.0000		TD(B3LYP)/aug-cc-pvdz
(HOMO→LUMO)	4.00			5.396			UOVGF/6-311+G*
	4.42						CIS/aug-cc-pvdz
	4.18	0.0694	2.70				CISD/aug-cc-pvdz
	4.02	0.0852	2.59	4.87	0.0000		TD(B3LYP)/aug-cc-pvdz
	4.12	0.0049					CASSCF(13,12)/6-311+G*
	4.01						CASPT2(13,12)/6-311+G*
(HOMO→LUMO+1)	7.76			7.56			UOVGF/6-311+G*
	8.58			4.98			CIS/aug-cc-pvdz
	7.73	0.0067	5.00	5.46	0.0000		CISD/aug-cc-pvdz
	6.74	0.0045	4.35				TD(B3LYP)/aug-cc-pvdz
(HOMO→LUMO+2)	7.99			6.10			UOVGF/6-311+G*
(HOMO→LUMO+3)	8.84			9.13			UOVGF/6-311+G*

(HOMO→LUMO+4)	8.85			8.89			UOVGF/6-311+G*
(HOMO→LUMO+5)	9.21			8.97			UOVGF/6-311+G*
(HOMO→LUMO+6)	8.77			9.22			UOVGF/6-311+G*
(HOMO→LUMO+7)	9.59			9.44			UOVGF/6-311+G*
(HOMO→LUMO+8)	9.48			9.40			UOVGF/6-311+G*
(HOMO→LUMO+9)	9.98			9.90			UOVGF/6-311+G*
(HOMO→LUMO+10)	10.08			10.27			UOVGF/6-311+G*
(HOMO→LUMO+11)	10.60			10.78			UOVGF/6-311+G*
(HOMO→LUMO+12)	11.02			10.97			UOVGF/6-311+G*
(HOMO→LUMO+13)	11.19			10.87			UOVGF/6-311+G*
(HOMO→LUMO+14)	10.36			11.14			UOVGF/6-311+G*
(HOMO→LUMO+15)	11.53			11.66			UOVGF/6-311+G*

Table S4. Excitation energies (E_e, in eV) and oscillator strengths (*f*) for 1,3-CHD^{2+} and 1,4-CHD^{2+} calculated at various level of theory, (λ = 1.55 eV).

Transition	E_e, 1,3-CHD^{2+}	*f*	E_e/λ	E_e, 1,4-CHD^{2+}	*f*	E_e/λ	Method
(HOMO→LUMO)		-		3.68	0.0717		CASSCF(13,12)/6-311+G*
		-		3.42			CASPT2(13,12)/6-311+G*
	2.72	-		0.90			UOVGF/6-311+G*
	-	-		2.00			CIS/aug-cc-pvdz
	-	-		3.38	0.2196	2.18	CISD/aug-cc-pvdz
	2.16	0.0016		2.08	0.0643	1.34	TD(B3LYP)/aug-cc-pvdz
(HOMO→LUMO,	4.16						CIS/aug-cc-pvdz
HOMO-3→LUMO)	3.50	0.1390	2.26				CISD/aug-cc-pvdz
(HOMO→LUMO+1)	5.92			8.07			CIS/aug-cc-pvdz
	5.85	0.0698		7.38	0.8495	4.76	CISD/aug-cc-pvdz
	6.15	0.0012		7.50	0.3914	4.84	TD(B3LYP)/aug-cc-pvdz
(HOMO→LUMO+2)				7.74	0.0000		TD(B3LYP)/aug-cc-pvdz
(HOMO→LUMO+3)				8.60			CIS/aug-cc-pvdz
				7.73	0.0000		CISD/aug-cc-pvdz
(HOMO→LUMO+6)				4.30			CIS/aug-cc-pvdz
				5.09	0.0000		CISD/aug-cc-pvdz
				4.09	0.0000		TD(B3LYP)/aug-cc-pvdz
(HOMO-1→LUMO)	3.00			2.23			UOVGF/6-311+G*
	3.61			2.50			CIS/aug-cc-pvdz
	2.68	0.0009		2.35	0.0000		CISD/aug-cc-pvdz
				1.69	0.0000		TD(B3LYP)/aug-cc-pvdz
(HOMO-1→LUMO, HOMO-2→LUMO)	3.72	0.1121	2.40				TD(B3LYP)/aug-cc-pvdz
(HOMO-1→LUMO+1)				8.88	0.0087		CASSCF(13,12)/6-311+G*

				8.49			CIS/aug-cc-pvdz
				7.92	0.0010		CISD/aug-cc-pvdz
	7.43	0.1819	4.79	7.24	0.0021		TD(B3LYP)/aug-cc-pvdz
(HOMO-1→LUMO+2)				8.03	0.0000		TD(B3LYP)/aug-cc-pvdz
(HOMO-2→LUMO+1)	6.64	0.0118		8.50	0.0000		TD(B3LYP)/aug-cc-pvdz
(HOMO-3→LUMO+1)	7.87	0.0600	5.08				TD(B3LYP)/aug-cc-pvdz
(HOMO-4→LUMO+1)	8.03	0.0423					TD(B3LYP)/aug-cc-pvdz
				4.43	0.0022		CASSCF(13,12)/6-311+G*
				4.34			CASPT2(13,12)/6-311+G*
(HOMO-2→LUMO)	5.94			4.25			CIS/aug-cc-pvdz
	4.08	0.0417		3.62	0.0142	2.34	CISD/aug-cc-pvdz
	2.64	0.0031		3.25	0.0066	2.10	TD(B3LYP)/aug-cc-pvdz
				4.06	0.0014		CASSCF(13,12)/6-311+G*
				3.62			CASPT2(13,12)/6-311+G*
(HOMO-3→LUMO)	4.31			6.48			CIS/aug-cc-pvdz
	3.84	0.1673		5.96	0.0883	3.85	CISD/aug-cc-pvdz
	4.34	0.0647	2.8	5.50	0.1482	3.55	TD(B3LYP)/aug-cc-pvdz
				5.17			CASPT2(13,12)/6-311+G*
(HOMO-4→LUMO)	6.04			5.03			CIS/aug-cc-pvdz
	4.35	0.0330		4.49	0.0000		CISD/aug-cc-pvdz
	3.97	0.0040		3.83	0.0000		TD(B3LYP)/aug-cc-pvdz
				3.45	0.0007		MCSCF(13,12)/6-311+G*
				3.14			CASPT2(13,12)/6-311+G*
(HOMO-5→LUMO)	6.74			7.62			CIS/aug-cc-pvdz
	5.33	0.0058		5.79	0.0000		CISD/aug-cc-pvdz
	5.73	0.0309		4.56	0.0000		TD(B3LYP)/aug-cc-pvdz
(HOMO-6→LUMO)	6.62			5.52			CIS/aug-cc-pvdz
	6.01	0.0026		5.36	0.0		CISD/aug-cc-pvdz
	5.27	0.0012		6.22	0.0000		TD(B3LYP)/aug-cc-pvdz
(HOMO-7→LUMO)	6.78			6.91			CIS/aug-cc-pvdz

	6.10 5.61	0.0104 0.0042		5.92 5.49	0.0000 0.0000		CISD/aug-cc-pvdz TD(B3LYP)/aug-cc-pvdz
(HOMO-8→LUMO)	7.17	0.0156		6.45	0.0000		TD(B3LYP)/aug-cc-pvdz
(HOMO-9→LUMO)	 7.53	 0.0763	 4.84	10.00 7.64 7.16	 0.0036 0.0000		CIS/aug-cc-pvdz CISD/aug-cc-pvdz TD(B3LYP)/aug-cc-pvdz
(LUMO→LUMO+1)	2.53 4.42 4.18 4.02	 0.0694 0.0852	 2.70 2.59	0.62 4.87	 0.0000		UOVGF/6-311+G* CIS/aug-cc-pvdz CISD/aug-cc-pvdz TD(B3LYP)/aug-cc-pvdz
(LUMO→LUMO+2)	6.88			6.66			UOVGF/6-311+G*
(LUMO→LUMO+3)	11.11			9.45			UOVGF/6-311+G*
(LUMO→LUMO+4)	9.85			7.32			UOVGF/6-311+G*
(LUMO→LUMO+5)	12.12			11.30			UOVGF/6-311+G*
(LUMO→LUMO+6)	12.87			11.20			UOVGF/6-311+G*
(LUMO→LUMO+7)	13.16			11.33			UOVGF/6-311+G*

Table S5. Relative energies of the ring opening and decomposition reactions (ΔE, kcal/mol) and corresponding transition states (ΔE(TS), kcal/mol) for the cyclohexadiene radical cation, dication in the singlet state, and $C_6H_7^+$.

Isomer, fragmentation channel	ΔE	ΔE(TS)	Level of calculations
$C_6H_8^+$			
1$^+$ (1,3-CHD$^+$)	0		B3LYP/6-31G**
	0		B3LYP/6-31G** +ZPE
	0		QCISD(T)/6-311G**//QCISD/6-31G*[37]
	0		UMP2/6-311+G**// UMP2/6-31G*[39,47]
5$^+$	23.7	39.9(TS_{15}) 35.3(TS_{58})	B3LYP/6-31G** + ZPE
	25.7	36.7(TS_{15}) 35.5(TS_{58})	QCISD(T)/6-311G**//QCISD/6-31G*[37]
8$^+$	18.6		B3LYP/6-31G** + ZPE
	21.5	36.9(TS_{18})	QCISD(T)/6-311G**//QCISD/6-31G*[37]
9$^+$	12.7	30.6(TS_{89})	B3LYP/6-31G** + ZPE
	16.8	31.0(TS_{89})	QCISD(T)/6-311G**//QCISD/6-31G*[37]
10$^+$	9.9	37.5(TS_{910})	B3LYP/6-31G** + ZPE
	14.2	48.0(TS_{910})	QCISD(T)/6-311G**//QCISD/6-31G*[37]
2$^+$ (1,4-CHD$^+$)	13.6		B3LYP/6-31G**
	11.9		B3LYP/6-31G** +ZPE
	12.0		G3MP2// B3LYP/6-31G**
	9.8		UMP2/6-311+G**//UMP2/6-31G*[39,47]
3$^+$	27.4	32.1(TS_{13})	B3LYP/6-31G**
	24.7	29.2(TS_{13})	B3LYP/6-31G** +ZPE
	23.0	26.8(TS_{13})	G3MP2// B3LYP/6-31G**
	23.9	35.5(TS_{13})	UMP2/6-311+G**//UMP2/6-31G*[39,47]
4$^+$	21.0	27.6(TS_{34})	B3LYP/6-31G**
	20.6	25.5(TS_{34})	B3LYP/6-31G** +ZPE
	11.0	25.0(TS_{34})	UMP2/6-311+G**//UMP2/6-31G*[39,47]
$C_6H_8^+$(**1**$^+$)→H+$C_6H_7^+$	52.4	52.4(TS_{111})	B3LYP/6-31G**
	45.7	46.2(TS_{111})	B3LYP/6-31G** +ZPE
	41.3	41.0(TS_{111})	G3MP2// B3LYP/6-31G**
	38.9	49.5(TS_{111})	UMP2/6-311+G**//UMP2/6-31G*[39,47]
$C_6H_8^+$(**1**$^+$)→H_2 + $C_6H_6^+$	57.3	57.4	B3LYP/6-31G(d,p)
	50.9	58.8	G3MP2// B3LYP/6-31G**
$C_6H_8^+$(**1**$^+$)→$C_4H_6^+$+C_2H_2	78.8		B3LYP/6-31G**
	75.0	74.2	B3LYP/6-31G(d,p) +ZPE
	78.4		UMP2/6-311+G**//UMP2/6-31G*[39,47]
	69.4	71.7	G3MP2// B3LYP/6-31G**

$C_6H_8^+$(**1**$^+$)→$C_2H_3^+$+C_4H_5	113.7		B3LYP/6-31G(d,p)
$C_6H_8^+$(**1**$^+$)→CH_3^++C_5H_5	115.3		B3LYP/6-31G(d,p)
$C_6H_7^+$			
$C_6H_7^+$→H+$C_6H_6^+$	64.9		B3LYP/6-31G(d,p) +ZPE
$C_6H_7^+$→H^++C_6H_6	176.0		B3LYP/6-31G(d,p) +ZPE
$C_6H_7^+$→H_2+$C_6H_5^+$	63.8		B3LYP/6-31G(d,p) +ZPE
$C_6H_6^+$→H+$C_6H_5^+$	92.7		B3LYP/6-31G(d,p) +ZPE
$C_6H_8^{2+}$			
1^{++} (1,3-CHD^{2+})	0 0		B3LYP/6-31G** +ZPE G3MP2// B3LYP/6-31G**
2^{++} (1,4-CHD^{2+})	18.8 18.3		B3LYP/6-31G** +ZPE G3MP2// B3LYP/6-31G**
3^{++}	-5.1 -5.7		B3LYP/6-31G** +ZPE G3MP2// B3LYP/6-31G**
$C_6H_8^{2+}$(**1**$^{++}$)→$C_3H_3^+$+ $C_3H_5^+$	-25.4 -27.3	56.0 57.1	B3LYP/6-31G(d,p) +ZPE G3MP2// B3LYP/6-31G**
$C_6H_8^{2+}$(**1**$^{++}$)→$C_2H_3^+$+ $C_4H_5^+$	-16.8 -19.3	57.5 56.9	B3LYP/6-31G(d,p) +ZPE G3MP2// B3LYP/6-31G**
$C_6H_8^{2+}$(**1**$^{++}$)→$C_4H_3^+$+ $C_2H_5^+$	-17.0 -26.1	56.8 60.2	B3LYP/6-31G(d,p) +ZPE G3MP2// B3LYP/6-31G**
$C_6H_8^{2+}$(**1**$^{++}$)→$C_5H_5^+$($^3D_{5h}$)+ CH_3^+	-17.1		B3LYP/6-31G(d,p) +ZPE
$C_6H_8^{2+}$(**1**$^{++}$)→$C_5H_5^+$($^1C_{2v}$)+ CH_3^+	-6.7		B3LYP/6-31G(d,p) +ZPE
$C_6H_8^{2+}$(**1**$^{++}$)→$C_5H_5^+$+ CH_3^+	-0.4 -3.5	58.5 57.6	B3LYP/6-31G(d,p) +ZPE G3MP2// B3LYP/6-31G**
$C_6H_8^{2+}$(**1**$^{++}$)→ $C_6H_7^+$+ H^+	42.3	77.2	B3LYP/6-31G(d,p) +ZPE
$C_6H_8^{2+}$(**1**$^{++}$)→ $C_6H_6^{++}$+ H_2	57.5	97.3	B3LYP/6-31G(d,p) +ZPE
$C_2H_5^+$($^1C_{2v}$) → $C_2H_3^+$+ H_2	52.3		B3LYP/6-31G(d,p) +ZPE
$C_2H_5^+$($^1C_{2v}$)→CH_3^++CH_2	150.5		B3LYP/6-31G(d,p) +ZPE
$C_2H_5^+$($^1C_{2v}$)→CH_3+CH_2^+	147.8		B3LYP/6-31G(d,p) +ZPE
$C_3H_5^+$($^1C_{2v}$) → $C_3H_3^+$+ H_2	56.2		B3LYP/6-31G(d,p) +ZPE
$C_3H_5^+$($^1C_{2v}$)→CH_2^++C_2H_3	176.8		B3LYP/6-31G(d,p) +ZPE
$C_4H_5^+$($^1C_{2v}$) → $C_4H_3^+$+ H_2	52.0		B3LYP/6-31G(d,p) +ZPE
$C_4H_5^+$($^1C_{2v}$)→$C_2H_3^+$+C_2H_2	83.1		B3LYP/6-31G(d,p) +ZPE
$C_4H_5^+$($^1C_{2v}$)→$^3C_2H^+$+C_2H_4	171.1		B3LYP/6-31G(d,p) +ZPE

Table S6. Relative energies (ΔE, kcal/mol) of various rotamers of hexatriene monocation with respect to the ttt rotamer **10**$^{+}$ and various rotamers of hexatriene dication with respect to the ttt rotamer **54**$^{++}$**.**

Isomer	ΔE	Level of calculation
5^{+}(ccc-HT)	14.2	ROHF/6-31G[41]
	14.0	CASSCF/6-31G[41]
	13.8	B3LYP/6-31G(d,p)+ZPE
8^{++}(ccc)	14.6	B3LYP/6-31G(d,p)+ZPE
13^{++}(ctc)	11.0	B3LYP/6-31G(d,p)+ZPE
8^{+}(cct-HT)	8.5	ROHF/6-31G[41]
	8.6	CASSCF/6-31G[41]
	8.7	B3LYP/6-31G(d,p)+ZPE
51^{++}(cct)	9.0	B3LYP/6-31G(d,p)+ZPE
12^{+}(ttc-HT)	3.8	ROHF/6-31G[41]
	3.4	CASSCF/6-31G[41]
	3.7	B3LYP/6-31G(d,p)+ZPE
40^{++}(ttc)	6.0	B3LYP/6-31G(d,p)+ZPE
9^{+}(tct-HT)	2.3	ROHF/6-31G [41]
	2.7	CASSCF/6-31G[41]
	2.8	B3LYP/6-31G(d,p)+ZPE
105^{++}(tct)	2.8	B3LYP/6-31G(d,p)+ZPE
10^{+}(ttt-HT)	0	ROHF/6-31G [41]
	0	CASSCF/6-31G[41]
	0	B3LYP/6-31G(d,p)+ZPE
54^{++}(ttt)	0	B3LYP/6-31G(d,p)+ZPE

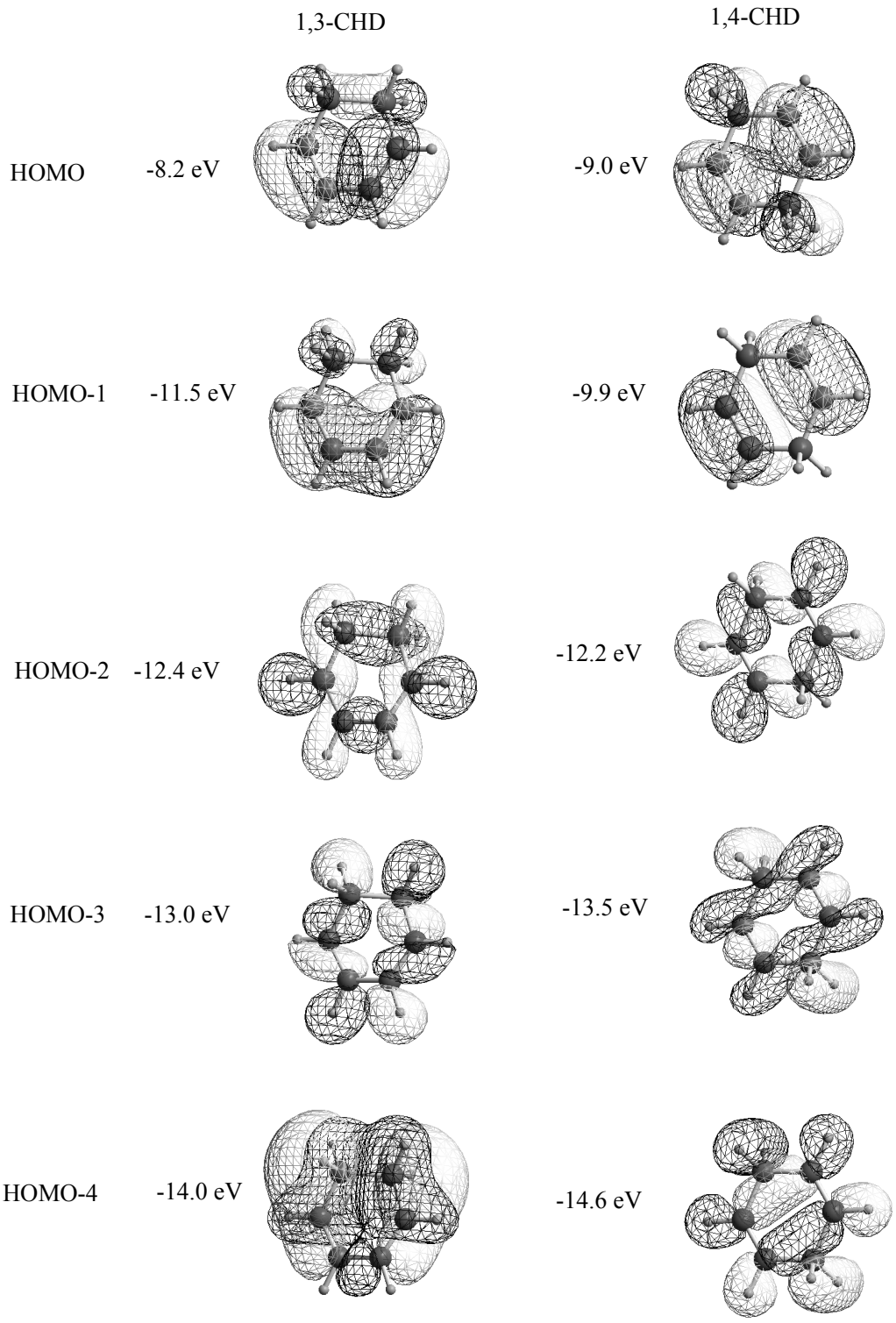

Fig. S1. Energy levels and electronic density distributions for the four highest occupied molecular orbitals in the 1,3-CHD and 1,4-CHD molecules calculated at the HF/6-311+G* level of theory.

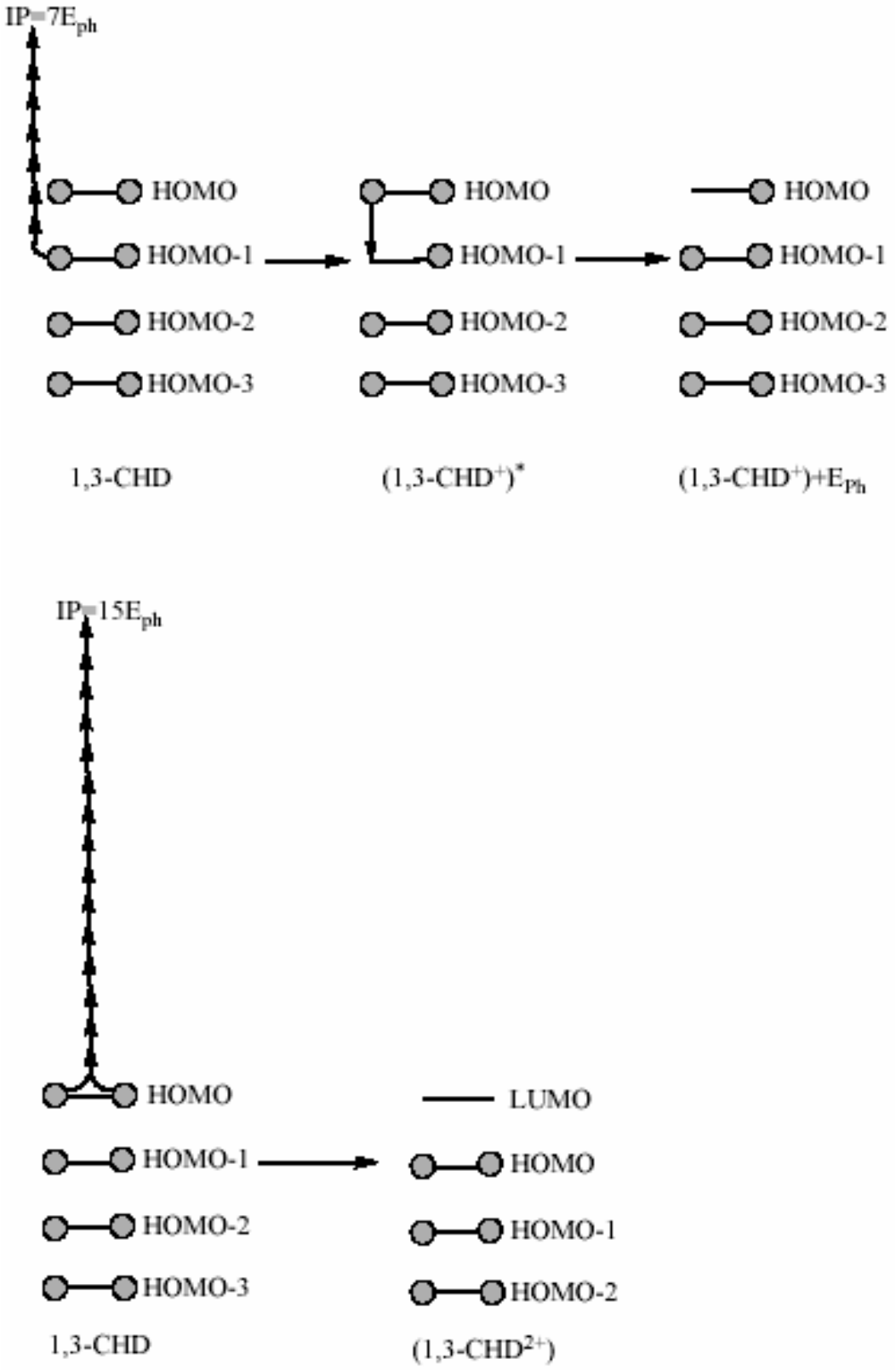

Fig. S2. Schematic presentation of ionization energies and molecular orbital levels involved in the formation of mono- and dications of 1,3-CHD.

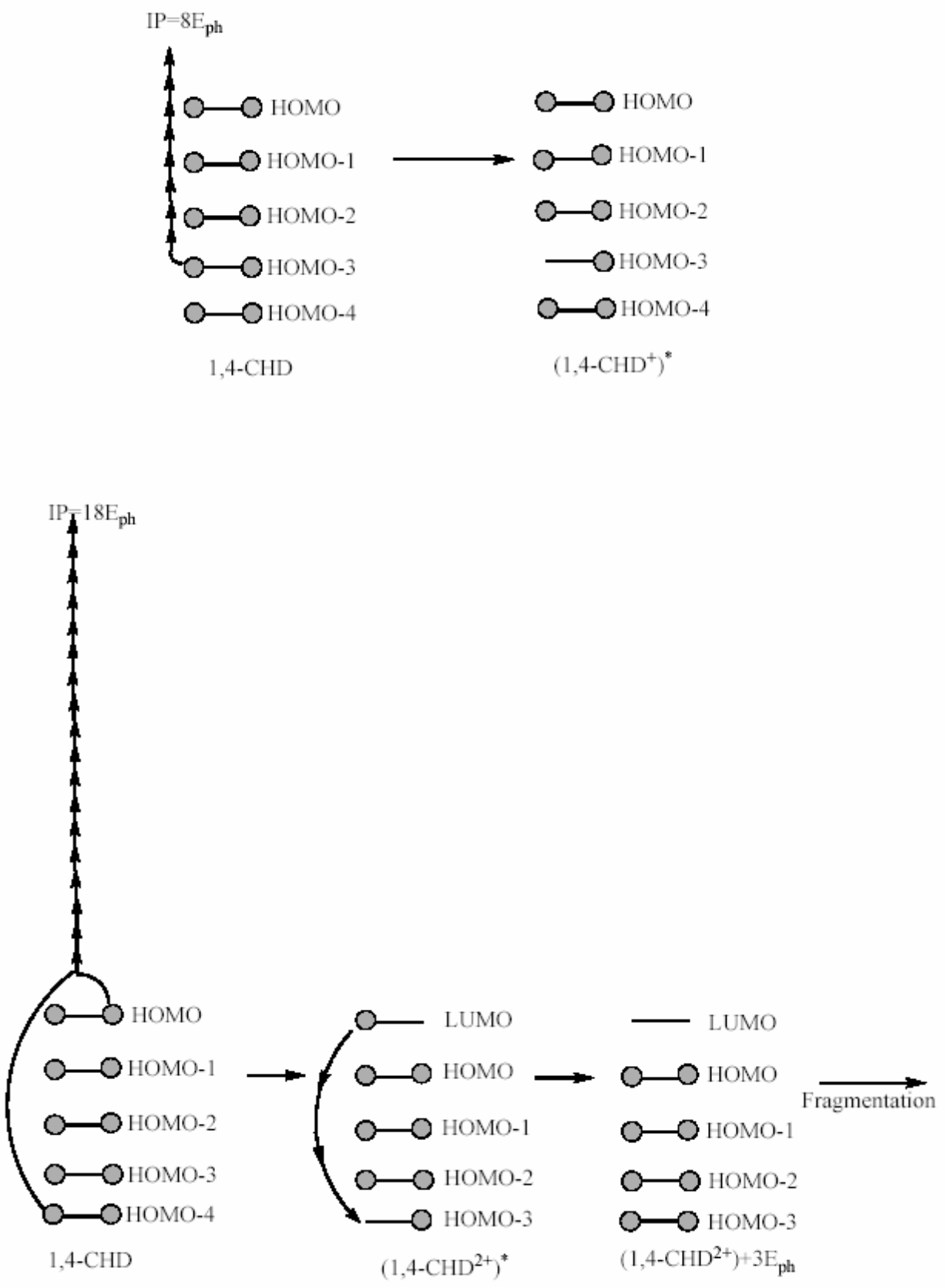

Fig. S3. Schematic presentation of ionization energies and molecular orbital levels involved in the formation of mono- and dications of 1,4-CHD.