ELECTRONIC SUPPLEMENTARY INFORMATION

DEC. 18, 2019

The Valence and Rydberg States of Dienes†

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Table S1. The Cartesian coordinates (Å) of 1,4-CHD

C	-0.00000000	1.24854019	-0.66259991
C	0.00000000	1.24854019	0.66259991
C	-0.00000000	-1.24854019	0.66259991
C	-0.00000000	-1.24854019	-0.66259991
H	-0.00000000	2.19226874	-1.19523456
H	0.00000000	2.19226874	1.19523456
H	-0.00000000	-2.19226874	1.19523456
H	-0.00000000	-2.19226874	-1.19523456
C	-0.00000000	-0.00000000	1.49286021
H	0.86754069	-0.00000000	2.16192650
H	-0.86754069	-0.00000000	2.16192650
C	-0.00000000	0.00000000	-1.49286021
H	-0.86754069	0.00000000	-2.16192650
H	0.86754069	0.00000000	-2.16192650

Table S2. The Cartesian coordinates (Å) of 1,3-CHD

C	0.070064	-1.421485	-0.050566
C	-0.070064	1.421485	-0.050566
C	0.131496	-0.722125	-1.203658
C	-0.131496	0.722125	-1.203658
C	0.272294	0.714489	1.254224
C	-0.272294	-0.714489	1.254224
H	0.270259	-2.484012	-0.091573
H	-0.270259	2.484012	-0.091573
H	0.371799	-1.192993	-2.147725
H	-0.371799	1.192993	-2.147725
H	-1.334908	-0.640484	1.355593
H	1.334908	0.640484	1.355593
H	0.197107	-1.317504	2.003180
H	-0.197107	1.317504	2.003180

Table S3. The main configurations of each state for 1,4-CHD after A′6-(4,6), A″(6)-(4,8), and the corresponding XMS-CASPT2 calculation.

State[a]	Dominant configurations[b]	
	CASSCF	XMS-CASPT2
$1\,^1A'^{c}$	220000 (92.3%)	220000 (92.2%)
$2\,^1A'^{c}$ (HOMO → LUMO)	2u00d0 (91.7%)	2u00d0 (91.7%)
$1\,^1A''^{d}$ (HOMO → 3s)	0u0 2d000 (61.3%)	00u d2000 (37.4%) (HOMO−1 → $3p_y$) 0u0 2d000 (32.7%) (HOMO →3s)
$2\,^1A''^{d}$ (HOMO → $3p_z$)	u00 2d000 (77.9%)	u00 2d000 (63.2%) (HOMO → $3p_x$) u00 d2000 (32.0%) (HOMO−1 → $3p_x$)
$3\,^1A''^{d}$ (HOMO → $3p_y$)[e]	00u 2d000 (45.3%) (HOMO→3p) 0u0 d2000 (30.8%) (HOMO−1→ 3s)	00u 2d000 (45.4%) (HOMO →$3p_y$) 0u0 2d000 (24.2%) (HOMO →3s)
$4\,^1A''^{d}$ (HOMO−1 → 3s)[e]	0u0 d2000 (45.3%) (HOMO−1 → 3s) 00u 2d000 (36.4%) (HOMO→3p)	0u0 d2000 (52.5%) (HOMO−1 → 3s) 0u0 2d000 (37.5%) (HOMO →3s)
$3\,^1A'^{c}$ (HOMO → $3p_x$)	2ud000 (95.5%)	2ud000 (95.4%)
$4\,^1A'^{c}$ (HOMO−1 → LUMO)	u200d0 (88.4%)	u200d0 (88.4%)

[a]The assignment of each state is based on the CASSCF wave function.
[b]All the configurations with a weight larger than 20% are shown.
[c]The order of the orbitals is the same as is indexed in Figure S1 from orbital 21 to orbital 26. All the orbitals have a″ symmetry.
[d]The order of the orbitals is the same as is indexed in Figure S2 from orbital 21 to orbital 28. The first three orbitals have a′ symmetry. The remaining orbitals have a″ symmetry.
[e]Transition from HOMO−1 to 3s orbital is mixed with the transition from HOMO to 3p orbital.

Table S4. The main configurations of each state for 1,4-CHD after A′(3)-(4,4) and the corresponding XMS-CASPT2 calculation.

State[a]	Dominant configurations[b]	
	CASSCF	XMS-CASPT2
$1\,^1A'$[c]	2200 (95.8%)	2200 (95.8%)
$2\,^1A'$[c] (HOMO → LUMO)	2ud0 (98.0%)	2ud0 (98.0%)
$4\,^1A'$[c] (HOMO−1 → LUMO)	u2d0 (98.0%)	u2d0 (98.0%)

[a]The assignment of each state is based on the CASSCF wave function.
[b]All the configurations with a weight larger than 20% are shown.
[c]The order of the orbitals is the same as is indexed in Figure S3 from orbital 21 to orbital 24. All the orbitals have a″ symmetry.

Table S5. The main configurations of each state for 1,3-CHD after A(6)-(4,12), B(6)-(4,12) and the corresponding XMS-CASPT2 calculation.

State[a]	Dominant configurations[b]	
	CASSCF	XMS-CASPT2
$1\,^1A^c$	200000 200000 (89.5%)	200000 200000 (89.5%)
$1\,^1B^d$ (HOMO →LUMO)	u00000 2d0000 (64.0%)	u00000 2d0000 (73.6%) (HOMO →LUMO)
$2\,^1B^d$ (HOMO → $3p_y$)	u00000 20d000 (49.3%) u00000 2000d0 (42.3%)	u00000 20d000 (47.5%) u00000 2000d0 (42.2%)
$3\,^1B^d$ (HOMO → $3p_x$)	u00000 200d00 (48.6%) u00000 20000d (42.5%)	u00000 200d00 (62.8%)
$2\,^1A^c$ (HOMO → 3s)	u0000d 200000 (44.5%) (HOMO→3s) u000d0 200000 (23.8%) (HOMO→3s)	u0000d 200000 (62.5%) (HOMO → 3s) u0d000 200000 (23.0%) (HOMO → $3p_z$)
$3\,^1A^c$ (HOMO → $3p_z$)	u00d00 200000 (34.0%) (HOMO→$3p_z$) u0d000 200000 (31.6%) (HOMO→$3p_z$) u000d0 200000 (20.8%) (HOMO→3s)	u00d00 200000 (45.6%) (HOMO → $3p_z$) u000d0 200000 (38.6%) (HOMO → 3s)
$4\,^1A^c$ (valence)	000000 220000 (20.0%) ($HOMO^2$→$LUMO^2$) 200000 ud0000 (15.1%) (HOMO−1→LUMO) u0000d 200000 (19.0%) (HOMO→3s) u0d000 200000 (14.4%) (HOMO→$3p_z$)	000000 220000 (21.7%) ($HOMO^2$→$LUMO^2$) 200000 ud0000 (14.7%) (HOMO → $3p_z$) u0d000 200000 (31.7%) (HOMO → $3p_z$)

[a]The assignment of each state is based on the CASSCF wave function.
[b]All the configurations with a weight larger than 14% are shown.
[c]The order of the orbitals is the same as is indexed in Figure S4 from orbital 21 to orbital 32.
[d]The order of the orbitals is the same as is indexed in Figure S5 from orbital 21 to orbital 32.

Table S6. The main configurations of each state for 1,3-CHD after B-SS-(4,4), A(2)-(4,4) and the corresponding XMS-CASPT2 calculation.

State[a]	Dominant configurations[b]	
	CASSCF	XMS-CASpt
$1\,^1A$[c]	20 20 (86.8%)	20 20 (86.8%)
$1\,^1B$[d] (HOMO → LUMO)	u0 2d (64.0%)	u0 2d (73.6%) (HOMO → LUMO)
$4\,^1A$[c] (mixed)	00 22 (35.6%) ($HOMO^2$ → $LUMO^2$) 20 ud (28.3%) (HOMO−1 → LUMO) ud 20 (18.5%) (HOMO → LUMO+1)	00 22 (35.6%) ($HOMO^2$ →$LUMO^2$) 20 ud (28.3%) (HOMO−1 → LUMO) ud 20 (18.5%) (HOMO → LUMO +1)

[a]The assignment of each state is based on the CASSCF wave function.
[b]All the configurations with a weight larger than 14% are shown.
[c]The order of the orbitals is the same as is indexed in Figure S6 from orbital 21 to orbital 24.
[d]The order of the orbitals is the same as is indexed in Figure S7 from orbital 21 to orbital 24.

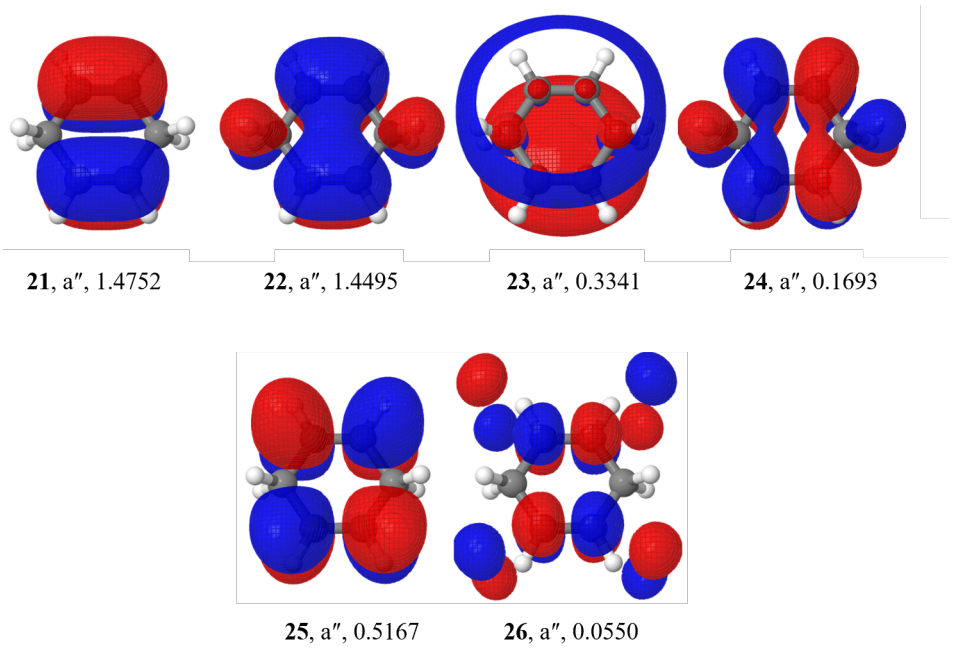


Figure S1. The active orbitals in A′(6)-(4,6) calculation for 1,4-CHD. Index, irreducible representation, and state-average occupation number are shown below each orbital. The density cutoff value for each orbital is 0.025 atomic units (a.u.).

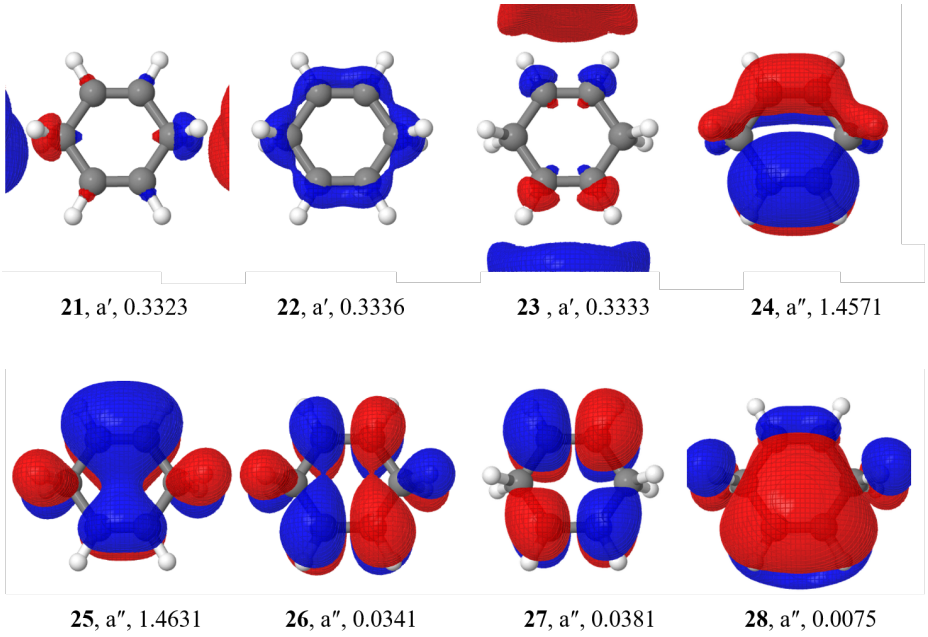
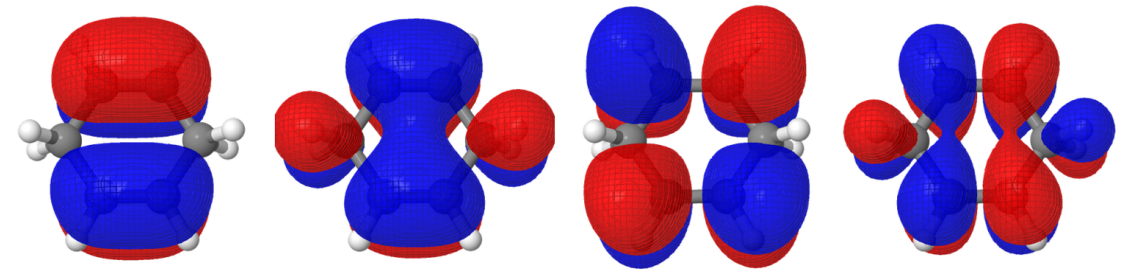


Figure S2. The active orbitals in A″(6)-(4,8) calculation for 1,4-CHD. Index, irreducible representation, and state-average occupation number are shown below each orbital. The density cutoff value for each orbital is 0.025 a.u.



21, a″, 1.6408 **22**, a″, 1.6470 **23**, a″, 0.6777 **24**, a″, 0.0346

Figure S3. The active orbitals in A′(3)-(4,4) calculation for 1,4-CHD. Index, irreducible representation, and state-average occupation number are shown below each orbital. The density cutoff value for each orbital is 0.025 a.u.

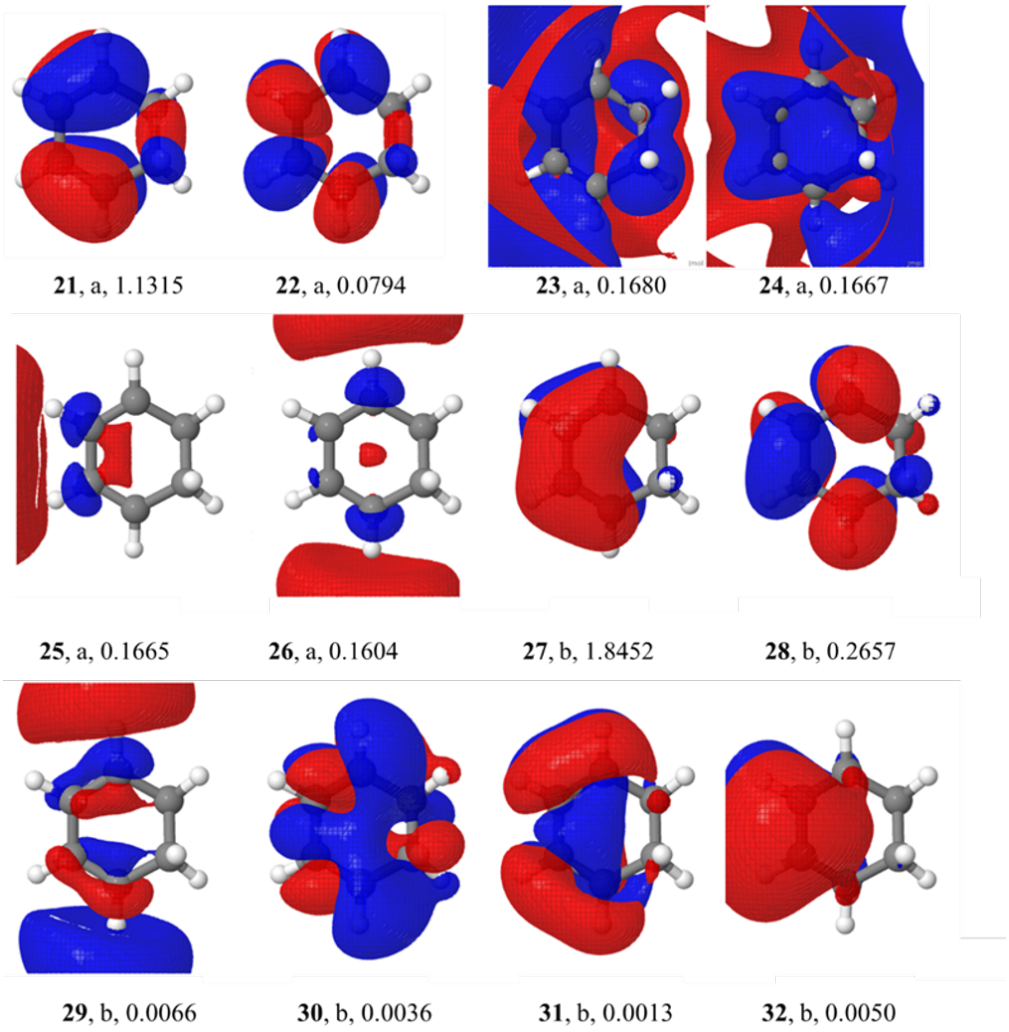


Figure S4. The active orbitals in A(6)-(4,12) calculation for 1,3-CHD. Index, irreducible representation, and state-average occupation number are shown below each orbital. The density cutoff value is 0.005 a.u.for orbital **23** and **24**, and 0.025 a.u. for all the other orbitals.

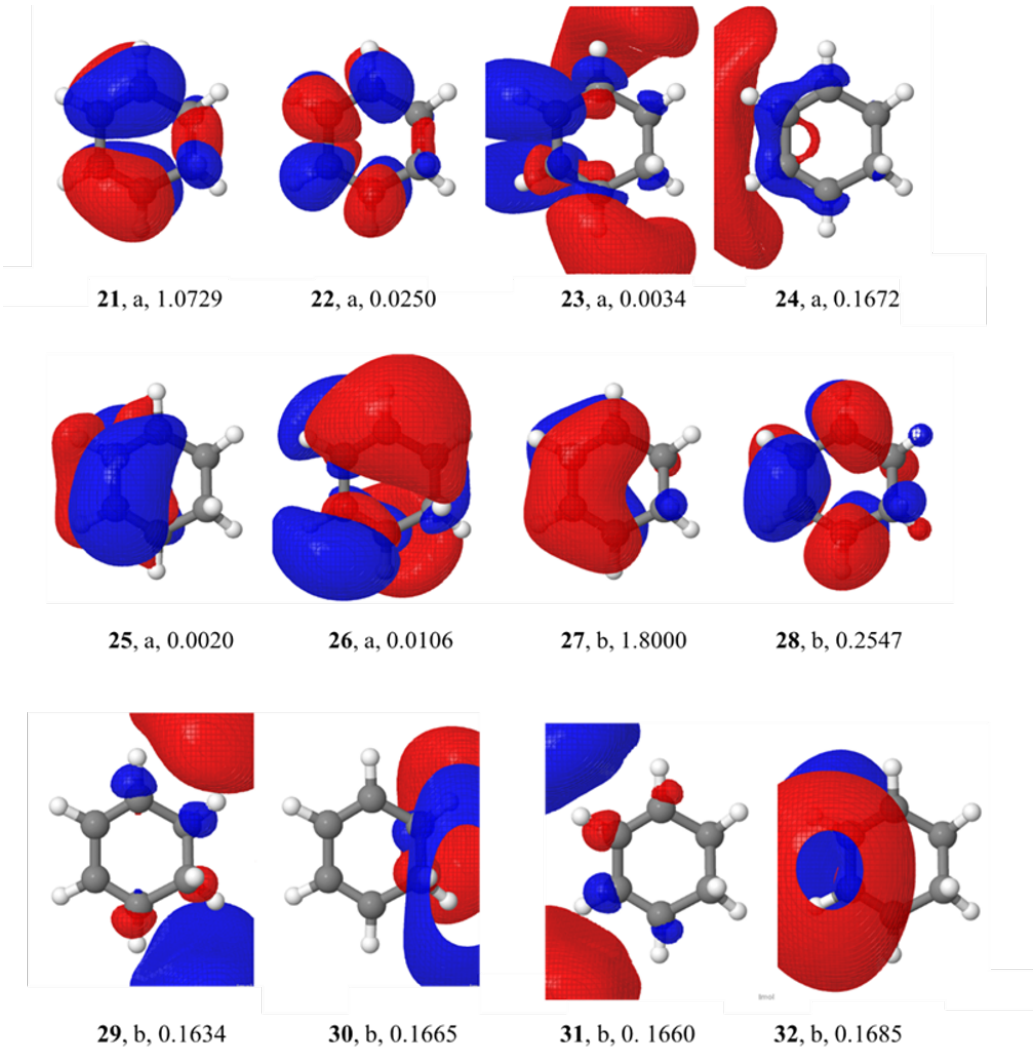
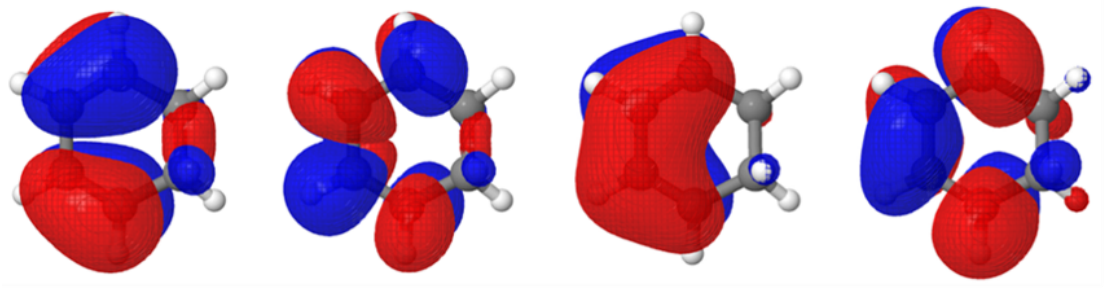


Figure S5. The active orbitals in B(6)-(4,12) calculation for 1,3-CHD. Index, irreducible representation, and state-average occupation number are shown below each orbital. The density cutoff value for each orbital is 0.025 a.u.



21, a, 1.4081 **22**, a, 0.2259 **23**, b, 1.7041 **24**, b, 0.6619

Figure S6. The active orbitals in A(2)-(4,4) calculation for 1,3-CHD. Index, irreducible representation, and occupation number are shown below each orbital. The density cutoff value for each orbital is 0.025 a.u.

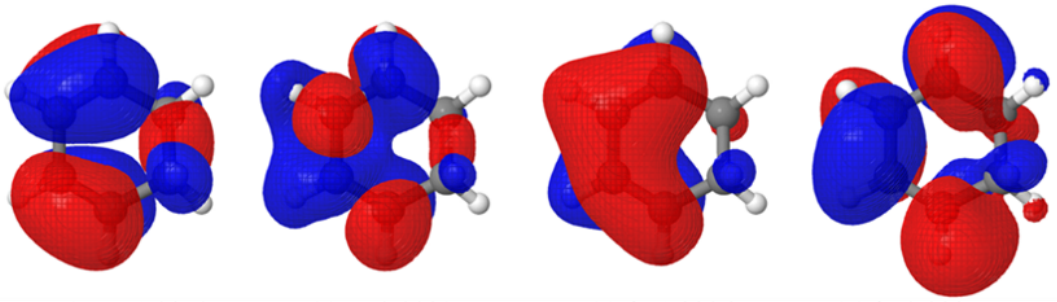


Figure S7. The active orbitals in B-SS-(4,4) calculation for 1,3-CHD. Index, irreducible representation, and occupation number are shown below each orbital. The density cutoff value for each orbital is 0.025 a.u.