Theoretical (DFT, GIAO-NMR, NICS) Study of Carbocations (M+H)⁺, Dications (M²⁺) and Dianions (M²⁻) from Dihydro-dicyclopenta[*ef,kl*]heptalene (Dihydro-azupyrene), Dihydro-dicyclohepta[*ed,gh*]pentalene, and Related Bridged [14]annulenes

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1.430 1.389

H

(H)

H

1.395

1.397

Ĥ





B

Î

1.408



Optimized geometries for 4, $4H^+$, $4aH^+$, $4bH^+$, triplet 4^{2+} , and singlet 4^{2-} at Fig S1. B3LYP/6-31G(d) level (bond length, Å).



Fig S1a. Optimized geometries for 4, $4bH^+$, triplet 4^{2+} , and singlet 4^{2-} at B3LYP/6-31+G(d,p) and B3LYP/6-31++G(d,p) levels (bond length, Å).





triplet 4²⁺ [B3LYP/6-31++G(d,p)]





Fig S1a (contined).



Fig S1b. Computed ¹³C NMR chemical shifts, NPA-derived carbon charges, and NPA-derived overall charges over CH units for **4bH**⁺, triplet **4**²⁺, and singlet **4**²⁻ ($\Delta\delta$ ¹³C's and Δ charges relative to **4** in parentheses) at B3LYP/6-31+G(d,p) level. [*Dark circles are roughly proportional to the magnitude of* $\Delta\delta$ ¹³Cs (positive/downfield for the carbocations/dication and negative/upfield for the dianion) ; threshold was set to 10 ppm].



Fig S1c. Computed ¹³C NMR chemical shifts, NPA-derived carbon charges, and NPA-derived overall charges over CH units for **4bH**⁺, triplet **4**²⁺, and singlet **4**²⁻ ($\Delta\delta$ ¹³C's and Δ charges relative to **4** in parentheses) at B3LYP/6-31++G(d,p) level. [*Dark circles are roughly proportional to the magnitude of* $\Delta\delta$ ¹³Cs (positive/downfield for the carbocations/dication and negative/upfield for the dianion); threshold was set to 10 ppm].



Fig S2. NICS values for $4H^+$, $4aH^+$, $4bH^+$, 4^{2+} , and 4^{2-} at B3LYP/6-31G(d), 6-31+G(d,p), or 6-31++G(d,p) level (Δ NICS values relative to those of 4 in parentheses).



Fig S3. B3LYP/6-31G(d) optimized geometries for 5, $5H^+$, $5aH^+$, $5bH^+$, 5^{2+} , and 5^{2-} (bond length, Å).





Fig S3 (continued).



Fig S4. Computed ¹³C NMR chemical shifts, NPA-derived carbon charges, and NPA-derived overall charges over CH units for $5H^+$, $5aH^+$, $5bH^+$, 5^{2+} , and 5^{2-} at B3LYP/6-31G(d) level ($\Delta\delta$ ¹³C's and Δ charges relative to 5 in parentheses). [*Dark circles are roughly proportional to the magnitude of* $\Delta\delta$ ¹³Cs (positive/downfield for the carbocations/dication and negative/upfield for the dianion); threshold was set to 10 ppm].







Fig S4 (continued).



Fig S5. NICS values for **5H**⁺, **5aH**⁺, **5bH**⁺, **5**²⁺, and **5**²⁻ at B3LYP/6-31G(d) or 6-31+G(d,p) level (Δ NICS values relative to those of **5** in parentheses).



Fig S6. B3LYP/6-31G(d) optimized geometries for 8, $8H^+$, triplet 8^{2+} , and singlet 8^{2-} (bond length, Å).





singlet 8²⁺



Fig S6 (continued).



Fig S7. NICS values for $\mathbf{8H}^+$, $\mathbf{8}^{2+}$, and $\mathbf{8}^{2-}$ at B3LYP/6-31G(d) or 6-31+G(d,p) level (Δ NICS values relative to those of **8** in parentheses).



Fig S8. Computed ¹³C NMR chemical shifts, NPA-derived carbon charges, and NPA-derived overall charges over CH units for **9H**⁺, **9**²⁺, and **9**²⁻ at B3LYP/6-31G(d) level ($\Delta\delta$ ¹³C's and Δ charges relative to **9** in parentheses). [*Dark circles are roughly proportional to the magnitude of* $\Delta\delta$ ¹³Cs (positive/downfield for the carbocations/dication and negative/upfield for the dianion); threshold was set to 10 ppm].



Fig S9. B3LYP/6-31G(d) optimized geometries for 9, $9H^+$, triplet 9^{2+} , and singlet 9^{2-} (bond length, Å).



Fig S10. NICS values for $9H^+$, 9^{2+} , and 9^{2-} at B3LYP/6-31G(d) or 6-31+G(d,p) level (Δ NICS values relative to those of 9 in parentheses).









singlet 10²⁺

singlet 10²⁻

Fig S11. B3LYP/6-31G(d) optimized geometries for 10, $10aH^+$, singlet 10^{2+} , and singlet 10^{2-} (bond length, Å).











Fig S12. B3LYP/6-31G(d) optimized geometries for **11**, **11H**⁺, singlet 11^{2+} , and singlet 11^{2-} and X-ray structure for **11** (bond length, Å).



Fig S13. Computed ¹³C NMR chemical shifts, NPA-derived carbon charges, and NPA-derived overall charges over CH units for $10aH^+$, 10^{2+} , and 10^{2-} at B3LYP/6-31G(d) level ($\Delta\delta$ ¹³C's and Δ charges relative to 10 in parentheses). [*Dark circles are roughly proportional to the magnitude of* $\Delta\delta$ ¹³Cs (positive/downfield for the carbocations/dication and negative/upfield for the dianion); threshold was set to 10 ppm].

B3LYP/6-311++G(3df,3pd)//B3LYP/6-31G(d) B3LYP/6-31+G(d,p)//B3LYP/6-31G(d) 157.6 (24.2) (4.1) 137.5 145.3 (22.1) (3.2) 126.4 Ĥ Η 45.1 40.1 (30.3) 160.0 (28.8) 148.3 н <u>H</u> 180.3 (41.2) н Н (3.6) 142.7 166.8 (38.8) (4.2) 132.2 59.7 (11.0) 54.5 (10.7) 140.9 (1.1) (9.1) 148.9 129.1 (2.0) (9.7) 136.8 55.6 (6.9) 50.7 (6.9) 168.4 (29.3) (5.4) 144.5 (4.7) 132.7 155.3 (27.3) Ĥ Ĥ (18.8) 148.6 (16.8) 136.4 132.1 (2.4) 121.8 (2.3) (6.7) 140.1 160.0 (26.6) (6.6) 129.8 147.3 (24.1) B3LYP/6-311++G(d,p)//B3LYP/6-31G(d) B3LYP/6-311++G(d,p)//B3LYP/6-311++G(d,p) 156.5 (23.1) (3.9) 137.9 156.8 (22.8) (3.8) 137.3 Н н 43.6 44.3 (28.9) 158.9 (29.0) 158.4 Н н 178.9 (41.1) 179.0 (40.7) (4.2) 142.4 (3.9) 141.7 59.4 (11.5) 58.9 (11.5) 140.7 (1.3) 140.0 (1.1) (9.5) 148.4 (9.5) 148.8 55.0 (7.1) 54.4 (7.1) 166.4 (28.6) 166.8 (28.5) (5.7) 143.5 (5.6) 143.9 Ĥ Н (18.9) 148.4 132.0 (2.5) (19.2) 149.2 132.6 (2.6) (6.7) 140.7 160.1 (26.1) (6.7) 140.2 159.7 (26.3) Experimental- $\delta^{13}C$ B3LYP/6-31G(d)//B3LYP/6-31G(d) (in superacid solution) 149.6 (23.1) (5.3) 131.8 142.0 (21.3) (3.4) 124.1 Ĥ (28.7) 151.5 28.8 37.9 (28.4) 145.2 Н Н (23.3) 154.8 185.5 (54.0) 162.6 (39.7) (5.0) 127.9 57.3 (14.3) 52.0 (11.7) 129.5 (-2.9) (10.5) 142.9 (8.8) 134.8 127.1 (1.0) 61.9 (18.9) 47.6 (7.3) (22.9) 154.4 157.9 (26.4) (6.7) 129.6 51.4 (28.5) Н Ē 131.8 (9.0) (28.7) 151.5 (17.6) 134.5 119.8 (2.9) (6.7) 127.4 145.1 (24.4) (2.2) 128.7 149.6 (23.1)

GIAO-δ¹³C

Fig S13a. Experimental (Ref 22) and computed ¹³C NMR chemical shifts for 10aH⁺.

 $10aH^+$

Figure S13b. Plots of experimental δ^{13} C vs GIAO-derived δ^{13} C and experimental $\Delta\delta^{13}$ C vs GIAO-derived $\Delta\delta^{13}$ C for **10aH**⁺ by ($^{\bigcirc}$) B3LYP/6-31G(d)//B3LYP/6-31G(d), ($^{\bullet}$) B3LYP/6-31+G(d,p)//B3LYP/6-31G(d), ($^{\times}$) B3LYP/6-311++G(3df,3pd)//B3LYP/6-31G(d), ($^{\bullet}$) B3LYP/6-311++G(d,p)//B3LYP/6-31G(d), ($^{\bullet}$) B3LYP/6-311++G(d,p)//B3LYP/6-31G(d), ($^{\bullet}$)

Fig S14. Computed ¹³C NMR chemical shifts, NPA-derived carbon charges, and NPA-derived overall charges over CH units for $11aH^+$, 11^{2+} , and 11^{2-} at B3LYP/6-31G(d) level ($\Delta\delta$ ¹³C's and Δ charges relative to 11 in parentheses). [*Dark circles are roughly proportional to the magnitude of* $\Delta\delta$ ¹³Cs (positive/downfield for the carbocations/dication and negative/upfield for the dianion); threshold was set to 10 ppm].

Fig S15. NICS values for $10aH^+$, 10^{2+} , and 10^{2-} at B3LYP/6-31G(d) or 6-31+G(d,p) level (Δ NICS values relative to those of 10 in parentheses).

Fig S16. NICS values for $11aH^+$, 11^{2+} and 11^{2-} at B3LYP/6-31G(d) or 6-31+G(d,p) level (Δ NICS values relative to those of 11 in parentheses).

14H⁺

singlet 14²⁺

singlet 14²⁻

Fig S17. B3LYP/6-31G(d) optimized geometries for **14**, **14H**⁺, singlet **14**²⁺ and singlet **14**²⁻ and X-ray structure for **14** (bond length, Å).

singlet 15²⁺

1.407

1.500

.507

1.514

.509

1.383

1.410

1.391

1.399

1.402

Ð

1.375

с Æ

1.377

1.389

Y

1.404

P

.522 1.50

Fig S18. B3LYP/6-31G(d) optimized geometries for 15, 15H⁺, 15aH⁺, singlet 15²⁺, and singlet 15^{2-} and X-ray structure for 15 (bond length, Å).

Fig S19. Computed ¹³C NMR chemical shifts, NPA-derived carbon charges, and NPA-derived overall charges over CH units for $14H^+$, 14^{2+} , and 14^{2-} at B3LYP/6-31G(d) level ($\Delta\delta$ ¹³C's and Δ charges relative to 14 in parentheses). [*Dark circles are roughly proportional to the magnitude of* $\Delta\delta$ ¹³Cs (positive/downfield for the carbocations/dication and negative/upfield for the dianion); threshold was set to 10 ppm].

Fig S20. Experimental (Ref 22) and computed ¹³C NMR chemical shifts for 14H⁺.

Figure S20a. Plots of experimental δ^{13} C vs GIAO-derived δ^{13} C and experimental $\Delta\delta^{13}$ C vs GIAO-derived $\Delta\delta^{13}$ C for **14H**⁺ by ($^{\bigcirc}$) B3LYP/6-31G(d)//B3LYP/6-31G(d), ($^{\bullet}$) B3LYP/6-31+G(d,p)//B3LYP/6-31G(d), ($^{\times}$) B3LYP/6-311++G(3df,3pd)//B3LYP/6-31G(d), ($^{\bullet}$) B3LYP/6-311++G(d,p)//B3LYP/6-31G(d), ($^{\bullet}$) B3LYP/6-311++G(d,p)//B3LYP/6-311++G(d,p).

Fig S21. Experimental (Ref 22) and computed ¹³C NMR chemical shifts for singlet 14²⁺.

B3LYP/6-31+G(d,p)//B3LYP/6-31G(d)

2+

39.1 (12.5) 148.9 (25.5)

162.4 (28.3)

137.8 (34.4)

146.9 (15.7)

2+

41.8 (12.9)

B3LYP/6-311++G(3df,3pd)//B3LYP/6-31G(d)

161.0 (26.3)

175.7 (29.8)

148.3 (36.1)

158.5 (15.2)

Figure S21a. Plots of experimental δ^{13} C vs GIAO-derived δ^{13} C and experimental $\Delta\delta^{13}$ C vs GIAO-derived $\Delta\delta^{13}$ C for 14²⁺ by ($^{\bigcirc}$) B3LYP/6-31G(d)//B3LYP/6-31G(d), ($^{\bullet}$) B3LYP/6-31+G(d,p)//B3LYP/6-31G(d), ($^{\times}$) B3LYP/6-311++G(3df,3pd)//B3LYP/6-31G(d), ($^{\bullet}$) B3LYP/6-311++G(3df,3pd)//B3LYP/6-31G(d), ($^{\bullet}$) B3LYP/6-311++(d,p)//B3LYP/6-311++G(d,p).

B3LYP/6-31+G(d,p)//B3LYP/6-31G(d)

Fig S21b. Experimental (Ref 21) and computed ¹³C NMR chemical shifts for singlet 14²⁻.

Figure S21c. Plots of experimental δ^{13} C vs GIAO-derived δ^{13} C and experimental $\Delta\delta^{13}$ C vs GIAO-derived $\Delta\delta^{13}$ C for 14²⁻ by ($^{\bigcirc}$) B3LYP/6-31G(d)//B3LYP/6-31G(d), ($^{\bullet}$) B3LYP/6-31+G(d,p)//B3LYP/6-31G(d), ($^{\times}$) B3LYP/6-311++G(3df,3pd)//B3LYP/6-31G(d), ($^{\bullet}$) B3LYP/6-311++G(d,p)//B3LYP/6-31G(d), ($^{\bullet}$) B3LYP/6-311++G(d,p)//B3LYP/6-31G(d), ($^{\bullet}$)

Fig S22. Computed ¹³C NMR chemical shifts, NPA-derived carbon charges, and NPA-derived overall charges over CH units for $15H^+$, $15aH^+$, 15^{2+} , and 15^{2-} at B3LYP/6-31G(d) level ($\Delta\delta$ ¹³C's and Δ charges relative to 15 in parentheses). [*Dark circles are roughly proportional to the magnitude of* $\Delta\delta$ ¹³Cs (positive/downfield for the carbocations/dication and negative/upfield for the dianion); threshold was set to 10 ppm].

Fig S22 (continued).

Fig S22a. Experimental (Ref 21) and computed ¹³C NMR chemical shifts for 15H⁺.

Figure S22b. Plots of experimental δ^{13} C vs GIAO-derived δ^{13} C and experimental $\Delta\delta^{13}$ C vs GIAO-derived $\Delta\delta^{13}$ C for **15H**⁺ by ($^{\bigcirc}$) B3LYP/6-31G(d)//B3LYP/6-31G(d), ($^{\bullet}$) B3LYP/6-31+G(d,p)//B3LYP/6-31G(d), ($^{\times}$) B3LYP/6-311++G(3df,3pd)//B3LYP/6-31G(d), ($^{\bullet}$) B3LYP/6-311++G(d,p)//B3LYP/6-31G(d), ($^{\bullet}$) B3LYP/6-311++G(d,p)//B3LYP/6-31G(d), ($^{\bullet}$)

Fig S22c. Experimental ¹H NMR chemical shifts for singlet **15²⁻** (Ref. 21).

164.6 (29.5)

180.3 (41.4)

151.6 (15.4)

148.8 (28.1)

B3LYP/6-31+G(d,p)//B3LYP/6-31G(d)

(17.3)

52.1

Figure S22e. Plots of experimental δ^{13} C vs GIAO-derived δ^{13} C and experimental $\Delta\delta^{13}$ C vs GIAO-derived $\Delta\delta^{13}$ C for **15²⁺** by ($^{\bigcirc}$) B3LYP/6-31G(d)//B3LYP/6-31G(d), ($^{\bullet}$) B3LYP/6-31+G(d,p)//B3LYP/6-31G(d), ($^{\times}$) B3LYP/6-311++G(3df,3pd)//B3LYP/6-31G(d), ($^{\bullet}$) B3LYP/6-311++G(d,p)//B3LYP/6-31G(d), ($^{\bullet}$) B3LYP/6-311++G(d,p)//B3LYP/6-31G(d), ($^{\bullet}$)

Fig S23. NICS values for 14^{2+} , 14^{2-} , 15^{2+} , and 15^{2-} at B3LYP/6-31G(d) or 6-31+G(d,p) level (Δ NICS values relative to those of parent hydrocarbons 14 and 15 in parentheses).

 $\delta^{13}C$ $\delta^{13}C$ Fig S24. Plots experimental vs GIAO-derived ofby (a) B3LYP/6-31+G(d,p)//B3LYP/6-31G(d), B3LYP/6-31G(d)//B3LYP/6-31G(d), (b) (c) B3LYP/6-311++G(d,p)//B3LYP/6-31G(d), (d) B3LYP/6-311++G(3df,3pd)//B3LYP/6-31G(d), (e) $B3LYP/6-311++G(d,p)//B3LYP/6-311++G(d,p) \ (\bigcirc: 10aH^+, \ \bullet: 14H^+, \ \times: \ singlet \ 14^{2+}, \ \Delta: \ singlet \ 14^{2+}, \$ 14²⁻, \blacktriangle : 15H⁺, \Box : singlet 15²⁺).

Addendum to Fig. S24

Computed δ^{13} C values correlate with the experimental data by equations (1-5) (see below) with R² = 0.94-0.95 and a slope of 0.89-0.96. The slopes at higher basic sets are closer to unity, although correlation coefficients R² are similar.

$$\begin{split} & \text{B3LYP/6-31(d)//B3LYP/6-31(d):} \\ & \delta^{13}\text{C} \ (\text{GIAO}) = 0.89 \times \delta^{13}\text{C} \ (\text{experimental}) + 6.4 & \text{R}^2 = 0.951 & (1) \\ & \text{B3LYP/6-31+G(d,p)//B3LYP/6-31G(d):} \\ & \delta^{13}\text{C} \ (\text{GIAO}) = 0.89 \times \delta^{13}\text{C} \ (\text{experimental}) + 10.2 & \text{R}^2 = 0.947 & (2) \\ & \text{B3LYP/6-311++G(d,p)//B3LYP/6-31G(d):} \\ & \delta^{13}\text{C} \ (\text{GIAO}) = 0.96 \times \delta^{13}\text{C} \ (\text{experimental}) + 11.3 & \text{R}^2 = 0.942 & (3) \\ & \text{B3LYP/6-311++G(3df,3pd)//B3LYP/6-31G(d):} \\ & \delta^{13}\text{C} \ (\text{GIAO}) = 0.95 \times \delta^{13}\text{C} \ (\text{experimental}) + 12.3 & \text{R}^2 = 0.940 & (4) \\ & \text{B3LYP/6-311++G(d,p)//B3LYP/6-311++G(d,p):} \\ & \delta^{13}\text{C} \ (\text{GIAO}) = 0.96 \times \delta^{13}\text{C} \ (\text{experimental}) + 11.4 & \text{R}^2 = 0.938 & (5) \\ \end{split}$$

HOMO for 4

LUMO for 4

Fig S25. Forms of HOMO, LUMO, and SOMO for 4, $4bH^+$, triplet 4^{2+} , and singlet 4^{2-} by B3LYP/6-31G(d).

Figure S25 (continued).

Figure S25 (continued).

Compd	Mole	cular E,	ZPE,	G,	ΔG,
	point	group hartree	hartree	hartree	kcal ^a
4	C ₁	-616.8707181	0.228341	-616.678445	(0)
6	C_1	-616.8465659	0.228190	-616.654624	14.9
5	C_1	-695.4919074	0.284632	-695.245566	(0)
7	C_1	-695.4536401	0.284425	-695.207700	23.8
8	C_1	-616.8234724	0.228569	-616.630880	(0)
10	C_1	-616.8738954	0.228787	-616.681047	-31.5
9	C_1	-695.4358718	0.283847	-695.190422	(0)
11	C_1	-695.5004848	0.284624	-695.254083	-39.9

Table S1. Energies (E), Zero Point Energies (ZPE), Gibbs Free Energies (G), and Relative Gibbs Free Energies (Δ G) for B3LYP/6-31G(d) Optimized Structures of Dihydro-derivatives **4-11**.

^a Relative Gibbs free energies of *syn*-derivatives to those of *anti*-derivatives.

Table S2. Energies (E), Zero Point Energies (ZPE), Gibbs Free Energies (G), Relative Gibbs Free Energies (Δ G) for B3LYP/6-31G(d) Optimized Structures for 4-5, 8-15, their Monocations, Dications, and Dianions

Compd	Protonation	Molecul	ar	Е,	ZPE,	G,	ΔG,	
	site	point gr	oup	hartree ^a	hartree ^a	hartree ^a	kcal ^b	
4		C ₁	-616.	8707181	0.228341	-616.678445	(0)	
		C_{2h}	-616.	8706817	0.228333	-616.677761	0.4	
$4H^+$	C(1)	C_1	-617.	2333368	0.240699	-617.029301	-220.2	
$4aH^+$	C(3)	C_1	-617.	234331	0.240751	-617.030422	-220.9	
$4bH^+$	C(4)	C_1	-617.	2384905	0.240730	-617.033830	-223.4	
$4^{2+}(s)^{c}$		C_1	-616.	2230611	0.228640	-616.031314	406.1	
		Ci	-616.	2230366	0.228626	-616.031306	406.1	
		C_{2h}^{d}	-616.	2214584	0.226870	-616.030650	406.5	
$4^{2+}(t)^{c}$		C_1	- 616.	2244602	0.228783	-616.033230	404.9	
		C_s	- 616.	2244602	0.228777	-616.033237		
		C_{2h}	-616.	2244166	0.228773	-616.032542	405.3	
$4^{2-}(s)^{c}$		C_1	-616.	7220175	0.218179	-616.540687	86.4	
		C_{2h}	-616.	7219216	0.218157	-616.539974	86.9	
$4^{2-}(t)^{c}$		C_1	-616.	7181169	0.217782	-616.538074	88.1	
		C_{2h}	-616.	7180712	0.217772	-616.537382	88.5	
5		C_1	-695.	4919074	0.284632	-695.245566	(0)	
		C_{2h}	-695.	4918974	0.284623	-695.244913	0.4	
$5H^+$	C(1)	C_1	-695.	8578678	0.296845	-695.599860	-222.3	
$5 \mathrm{aH}^+$	C(3)	C_1	-695.	8578801	0.296912	-695.600027	-222.4	
$5bH^+$	C(4)	C_1	-695.	8615373	0.297000	-695.603381	-224.5	
$5^{2+}(s)^{c}$		Ci	-694.	8542078	0.284409	-694.608866	399.5	
		C_{2h}^{d}	-694.	8534797	0.282958	-694.608601	399.7	
		C_1	-694.	8542025	0.284498	-694.608694	399.6	
$5^{2+}(t)^{c}$		C_{2h}	- 694.	8545546	0.284792	-694.608847	399.5	
		C_1	- 694.	8545828	0.284811	-694.609502	399.1	
$5^{2-}(s)^{c}$		C_{2h}	-695.	3532913	0.273662	-695.118077	80.0	
		C_1	-695.	3533188	0.273624	-695.118835	79.5	
$5^{2-}(t)^{c}$		C_{2h}	-695.	3467395	0.273701	-695.112390	83.6	
		C_1	-695.	3467665	0.273722	-695.113043	83.2	

^a 1 hartree = 627.5096 kcal/mol. ^b Relative Gibbs free energies to those of the parent hydrocarbons. ^c (s) and (t) denote triplet and singlet states. ^d Number of imaginary frequencies = 1.

Compd	Protonation	Molecu	lar	E,	ZPE,	G,	ΔG ,	
	site	point gr	oup	nartree	nartree	nartree	ксаг	
8		C _{2h}	-616.	8234939	0.228588	-616.630225	0.4	
		C_1	-616.	8234724	0.228569	-616.630880	(0)	
8H ⁺	C(5)	C_1	-617.	1897954	0.240435	-616.986002	-222.8	
$8 a H^+$	C(1)	C_1	-617.	1836447	0.240668	-616.979726	-218.9	
$8bH^+$	C(2)	C_1	-617.	1886921	0.240909	-616.984366	-221.8	
$8^{2+}(s)^{c}$		C_{2h}	-616.	1844352	0.229021	-615.991327	401.3	
		C_1	-616.	1844054	0.228991	-615.991986	400.9	
$8^{2+}(t)^{c}$		C_{2h}	-616.	1731913	0.228392	-615.981566	407.5	
		C_1	-616.	1731519	0.228345	-615.982242	407.0	
$8^{2}(s)^{c}$		C_{2h}	-616.	7091687	0.218790	-616.526239	65.7	
		C_1	-616.	7091512	0.218781	-616.526889	65.3	
$8^{2-}(t)^{c}$		C_{2h}	-616.	6988577	0.218887	-616.516534	71.8	
		C_1	-616.	6988251	0.218860	-616.517189	71.3	
9		C_{2h}	-695.	4358090	0.283771	-695.189819	0.4	
		C_1	-695.	4358718	0.283847	-695.190422	(0)	
9H ⁺	C(5)	C_1	-695.	8115965	0.296398	-695.554000	-228.1	
9aH ⁺	C(1)	C_1	-695.	7989077	0.295817	-695.542439	-220.9	
$9bH^+$	C(2)	C_1	-695.	8035653	0.295982	-695.546766	-223.6	
$9^{2+}(s)^{c}$		C_{2h}	-694.	8082124	0.284235	-694.562690	393.9	
		C_1	-694.	8081658	0.284146	-694.563478	393.4	
$9^{2+}(t)^{c}$		C_{2h}	-694.	7976001	0.283432	-694.553371	399.8	
		C_1	-694.	7975569	0.283357	-694.554107	399.3	
$9^{2}(s)^{c}$		$C_{2h}^{ \ b}$	-695.	3236722	0.273068	-695.088935	63.7	
		C_1	-695.	3238175	0.273755	-695.089723	63.2	
$9^{2-}(t)^{c}$		C_{2h}	-695.	3166255	0.274226	-695.081418	68.4	
		C_1	-695.	3166141	0.274213	-695.082080	68.0	

Table S2 (continued).

Table	S2	(continued).
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$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		ΔG,	G,	ZPE,	Е,	Molecular	Protonation	Compd
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		kcal ^b	hartree ^a	hartree ^a	hartree ^a	point group	site	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$								
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		0.4	-616.680393	0.228787	.8738954	C _{2v} -616		10
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		(0)	-616.681047	0.228787	.8738954	C ₁ -616		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		-216.4	-617.025966	0.240586	.2300612	C _s -617	C(5)	$10H^+$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		-216.4	-617.025967	0.240586	.2300612	C ₁ -617		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		-221.9	-617.034712	0.240969	.2391727	C ₁ -617	C(1)	$10 \mathrm{aH}^+$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		-220.1	-617.031813	0.240777	.235936	C ₁ -617	C(2)	$10 b H^+$
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		410.6	-616.026611	0.228383	.2188396	C _{2v} -616		$10^{2^{+}}(s)^{c}$
10^{2+} (t) ^c C _{2v} -616.21690670.228321-616.025267411.5C1-616.21690670.228321-616.025921411.1		410.3	-616.027265	0.228383	.2188396	C ₁ -616		
$C_1 \qquad -616.2169067 \qquad 0.228321 \qquad -616.025921 \qquad 411.1$		411.5	-616.025267	0.228321	.2169067	C _{2v} -616		$10^{2^{+}}(t)^{c}$
		411.1	-616.025921	0.228321	.2169067	C ₁ -616		
10^{2-} (s) ^c C _s -616.7470000 0.218961 -616.564409 73.2		73.2	-616.564409	0.218961	.7470000	C _s -616		10^{2} (s) ^c
C_1 -616.7469915 0.218991 -616.564379 73.2		73.2	-616.564379	0.218991	.7469915	C ₁ -616		
10^{2-} (t) ^c C _s -616.7283051 0.218584 -616.547035 84.1		84.1	-616.547035	0.218584	.7283051	C _s -616		$10^{2-}(t)^{c}$
$C_1 \qquad -616.7282851 \qquad 0.218561 \qquad -616.547050 \qquad 84.1$		84.1	-616.547050	0.218561	.7282851	C ₁ -616		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		0.4	-695.253430	0.284624	.5004848	C _{2v} -695		11
$C_1 \qquad -695.5004848 \qquad 0.284624 \qquad -695.254083 \qquad (0)$		(0)	-695.254083	0.284624	.5004848	C ₁ -695		
11H^+ C(5) C _s -695.8573173 0.296495 -695.599584 -216.8		-216.8	-695.599584	0.296495	.8573173	C _s -695	C(5)	$11H^+$
C_1 695.8573173 0.296495 -695.599584 -216.8		-216.8	-695.599584	0.296495	.8573173	C ₁ 695		
11aH ⁺ C(1) C ₁ -695.8675051 0.297025 -695.609250 -222.9		-222.9	-695.609250	0.297025	.8675051	C ₁ -695	C(1)	$11 \mathrm{aH}^+$
11bH ⁺ C(2) C ₁ -695.8636513 0.296574 -695.606023 -220.8		-220.8	-695.606023	0.296574	.8636513	C ₁ -695	C(2)	$11bH^+$
$11^{2+} (s)^{c} \qquad \qquad \mathbf{C}_{2v} \qquad -694.8508447 \qquad 0.284850 \qquad -694.604621 \qquad 407.5$		407.5	-694.604621	0.284850	.8508447	C _{2v} -694		$11^{2+}(s)^{c}$
$C_1 \qquad -694.8508447 \qquad 0.284850 \qquad -694.605275 \qquad 407.1$		407.1	-694.605275	0.284850	.8508447	C ₁ -694		
$11^{2+} (t)^{c} \qquad C_{2v} -694.8487787 0.284259 -694.603589 408.2$		408.2	-694.603589	0.284259	.8487787	C _{2v} -694		$11^{2+}(t)^{c}$
$C_1 \qquad -694.8487787 \qquad 0.284260 \qquad -694.604243 \qquad 407.8$		407.8	-694.604243	0.284260	.8487787	C ₁ -694		
11²⁻ (s) ^c C_{2v} -695.3740715 0.274706 -695.137263 73.3		73.3	-695.137263	0.274706	.3740715	C _{2v} -695		$11^{2-} (s)^{c}$
C_1 -695.3740715 0.274707 -695.137917 72.9		72.9	-695.137917	0.274707	.3740715	C ₁ -695		
11²⁻ (t) ^c C_{2v} -695.355764 0.274343 -695.120310 83.9		83.9	-695.120310	0.274343	.355764	C _{2v} -695		$11^{2-}(t)^{c}$
C_1 -695.355764 0.274344 -695.120963 83.5		83.5	-695.120963	0.274344	3.355764	C ₁ -695		

Compd	Protonation	Molecu	lar	Е,	ZPE	Ξ,		G,	Z	1G,	
	site	point gr	oup	hartree ^a	hart	ree ^a		hartree ^a	1	ccal ^b	
14		C_{2v}	-618.	0403323	0.252	2018	-6	17.82392	29	0.4	
		C_1	-618.	0403323	0.252	2019	-6	17.82458	83	(0)	
$14H^+$	C(5)	Cs	-618.	413039	0.264	4786	-6	18.18492	28 -2	226.1	
		C_1	-618.	413039	0.264	4786	-6	18.18492	28 -2	226.1	
$14aH^+$	C(1)	C_1	- 618.	4120941	0.264	4625	-6	18.18409	96 -2	225.6	
$14^{2+}(s)^{c}$		C_{2v}	- 617.	3963755	0.252	2767	-6	17.1793	55 4	404.9	
		C_1	- 617.	3963755	0.252	2767	-6	17.18000	09 4	404.5	
$14^{2+}(t)^{c}$		C_{2v}	- 617.	379102	0.251	302	-6	17.1648:	58 4	414.0	
		C_1	- 617.	379102	0.251	302	-6	17.1655	12 4	413.6	
$14^{2-}(s)^{c}$		C_{2v}	- 617.	904338	0.242	2016	-6	17.69850	59	79.1	
		C_1	- 617.	904338	0.242	2016	-6	17.69922	22	78.7	
$14^{2-}(t)^{c}$		C_{2v}	- 617.	8882346	0.241	606	-6	17.68372	25	88.4	
		C_1	- 617.	8882346	0.241	607	-6	17.6843	78	88.0	
15		C_{2v}	-656.	1807873	0.258	3796	-63	55.9576	11	0.4	
		C_1	-656.	1807873	0.258	3797	-63	55.95820	64	(0)	
$15H^+$	C(5)	Cs	-656.	5443439	0.271	000	-63	56.31004	41 -2	220.7	
		C_1	-656.	5443439	0.271	001	-63	56.31004	41 -2	220.7	
15aH ⁺	C(1)	C_1	-656.	5503302	0.271	170	-63	56.31590	06 -2	224.4	
$15^{2+}(s)^{c}$		C_{2v}	-655.	5347736	0.259	9031	-63	55.31158	32 4	405.8	
		C_1	-655.	5347736	0.259	9031	-63	55.31223	36 4	405.4	
$15^{2+}(t)^{c}$		C_{2v}	-655.	5213722	0.258	8087	-6.	55.30039	91 4	412.8	
		C_1	-655.	5213722	0.258	8088	-6.	55.30104	44 4	412.4	
$15^{2-}(s)^{c}$		C_{2v}	-656.	0498283	0.248	3739	-6.	55.83718	88	76.0	
		C_1	-656.	0498283	0.248	3740	-6:	55.83784	42	75.6	
$15^{2-}(t)^{c}$		C_{2v}	-656.	0312338	0.248	3407	-63	55.8198	51	86.9	
		C_1	-656.	0312338	0.248	3408	-63	55.82050	04	86.4	

Table S2 (continued).

Compd Protonation	site					
basic set	Molecular	Е,	ZPE,	G,	ΔG,	
	point grou	p hartree	hartree	hartree	kcal ^a	
4						
B3LYP/6-31G(d)	C ₁ -6	16.8707181	0.228341	-616.678445	(0)	
B3LYP/6-31+G(d,p)	C ₁ -6	16.9102648	0.227337	-616.719035	(0)	
B3LYP/6-31++G(d,p)	C ₁ -6	16.910426	0.227363	-616.719166	(0)	
4H ⁺ C(1)						
B3LYP/6-31G(d)	C ₁ -6	17.2333368	0.240699	-617.029301	-220.2	
B3LYP/6-31+G(d,p)	C ₁ -6	17.2653618	0.239618	-617.062429	-215.5	
B3LYP/6-31++G(d,p)	C ₁ -6	17.2655807	0.239627	-617.062637	-215.5	
$4aH^{+}$ C(3)						
B3LYP/6-31G(d)	C ₁ -6	17.234331	0.240751	-617.030422	-220.9	
B3LYP/6-31+G(d,p)	C ₁ -6	17.266431	0.239662	-617.063632	-216.2	
B3LYP/6-31++G(d,p)	C ₁ -6	17.2667051	0.239676	-617.063890	-216.3	
4bH ⁺ $C(4)$						
B3LYP/6-31G(d)	C ₁ -6	17.2384905	0.240730	-617.033830	-223.4	
B3LYP/6-31+G(d,p)	C ₂ -6	17.2705073	0.239629	-617.066981	-218.3	
B3LYP/6-31++G(d,p)	C ₂ -6	17.2707331	0.239645	-617.067190	-218.4	
$4^{2+}(s)$						
B3LYP/6-31G(d)	C ₁ -6	16.2230611	0.228640	-616.031314	406.1	
B3LYP/6-31+G(d,p)	C ₁ -6	16.2489933	0.227759	-616.058145	414.7	
B3LYP/6-31++G(d,p) 4 ²⁺ (t)	C ₁ -6	16.2492048	0.227777	-616.058331	414.7	
B3LYP/6-31G(d)	C ₁ -6	16.2244602	0.228783	-616.033230	404.9	
B3LYP/6-31+G(d,p)	C _s -6	16.2502732	0.227906	-616.059936	413.6	
B3LYP/6-31++G(d,p)	C _s -6	16.2505412	0.227939	-616.060160	413.5	
$4^{2-}(s)$						
B3LYP/6-31G(d)	C ₁ -6	16.7220175	0.218179	-616.540687	86.4	
B3LYP/6-31+G(d,p)	C _i -6	16.81053	0.218047	-616.629518	56.2	
B3LYP/6-31++G(d,p)	C _i -6	16.8154522	0.220108	-616.632721	54.2	
$4^{2-}(t)$						
B3LYP/6-31G(d)	C ₁ -6	16.7181169	0.217782	-616.538074	88.1	
B3LYP/6-31+G(d,p)	C ₁ -6	16.8027096	0.216199	-616.625230	58.9	
B3LYP/6-31++G(d,p)	$C_1 - 6$	16.8257125	0.221942 ^b	-616.640690	49.0	

Table S3. Energies (E), Zero Point Energies (ZPE), Gibbs Free Energies (G), Relative Gibbs Free Energies (Δ G) for Optimized Structures for 4, its Monocations, Dications, and Dianions

^a Relative energies to the neutral. ^b Number of imaginary frequency is 1.

Compd							
baisc set	Molecu	ular	Е,	ZPE,	G,	ΔG,	
	point g	roup	hartree	hartree	hartree	kcal ^a	
5							
B3LYP/6-31G(d)	C_1	-695	.4919074	0.284632	-695.245566	(0)	
B3LYP/6-31+G(d,p)	C_1	-695	.5373455	0.283160	-695.292516	(0)	
5²⁻ (s)							
B3LYP/6-31G(d)	C_1	-695	.3533188	0.273624	-695.118835	79.5	
B3LYP/6-31+G(d,p)	C_1	-695	.4453828	0.273100	-695.211455	50.9	
5 ²⁻ (t)							
B3LYP/6-31G(d)	C_1	-695	.3467665	0.273722	-695.113043	83.2	
B3LYP/6-31+G(d,p)	C_1	-695	.4356826	0.272290	-695.203664	55.8	
8							
B3LYP/6-31G(d)	C_1	-616	.8234724	0.228569	-616.630880	(0)	
B3LYP/6-31+G(d,p)	C_1	-616	.8639904	0.227603	-616.672389	(0)	
8²⁻ (s)							
B3LYP/6-31G(d)	C_1	-616	.7091512	0.218781	-616.526889	65.3	
B3LYP/6-31+G(d,p)	C_1	-616	.7911433	0.216601	-616.612105	37.8	
8²⁻ (t)							
B3LYP/6-31G(d)	C_1	-616	.6988251	0.218860	-616.517189	71.3	
B3LYP/6-31+G(d,p)	C_1	-616	.783247	0.217881	-616.602835	43.6	
9							
B3LYP/6-31G(d)	C_1	-695	.4358718	0.283847	-695.190422	(0)	
B3LYP/6-31+G(d,p)	C_1	-695	.4821086	0.282391	-695.238197	(0)	
9²⁻ (s)							
B3LYP/6-31G(d)	C_1	-695	.3238175	0.273755	-695.089723	63.2	
B3LYP/6-31+G(d,p)	C_1	-695	.4115526	0.272225	-695.178851	37.2	
9²⁻ (t)							
B3LYP/6-31G(d)	C_1	-695	.3166141	0.274213	-695.082080	68.0	
B3LYP/6-31+G(d,p)	C_1	-695	.4057966	0.272888	-695.172796	41.0	

Table S4. Energies for Optimized Structures for 5, 8, 9, 10, 11, 14, 15, and their dianions by B3LYP/6-31+G(d,p)

^b Relative Gibbs free energies to those of the parent hydrocarbons. ^b Number of imaginary frequencies = 1.

Compd						
baisc set	Molecul	ar	Е,	ZPE,	G,	ΔG,
	point gro	oup	hartree	hartree	hartree	kcal ^a
10						
B3LYP/6-31G(d)	C_1	-616.	8738954	0.228787	-616.681047	(0)
B3LYP/6-31+G(d,p)	C_1	-616.	913608	0.227808	-616.721778	(0)
10²⁻ (s)						
B3LYP/6-31G(d)	Cs	- 616.	7470000	0.218961	-616.564409	73.2
B3LYP/6-31+G(d,p)	C_1	- 616.	8305483	0.217839	-616.649253	45.5
10²⁻ (t)						
B3LYP/6-31G(d)	C_1	-616.	7282851	0.218561	-616.547050	84.1
B3LYP/6-31+G(d,p)	C_1	-616.	8136409	0.217338	-616.634063	55.0
11						
B3LYP/6-31G(d)	C_1	-695.	5004848	0.284624	-695.254083	(0)
B3LYP/6-31+G(d,p)	C_1	-695.	5468117	0.283283	-695.301795	(0)
11 ²⁻ (s)						
B3LYP/6-31G(d)	C_1	-695.	3740715	0.274707	-695.137917	72.9
B3LYP/6-31+G(d,p)	C_1	-695.	4634247	0.273319	-695.228806	45.8
11²⁻ (t)						
B3LYP/6-31G(d)	C_1	-695.	355764	0.274344	-695.120963	83.5
B3LYP/6-31+G(d,p)	C_1	-695.	4472602	0.272326 ^b	-695.214100	55.0
14						
B3LYP/6-31G(d)	C_1	-618.	0403323	0.252019	-617.824583	(0)
B3LYP/6-31+G(d,p)	C_1	-618.	0831353	0.250841	-617.868622	(0)
14 ²⁻ (s)						
B3LYP/6-31G(d)	C_1	-617.	904338	0.242016	-617.699222	78.7
B3LYP/6-31+G(d,p)	C_1	-617.	9946934	0.240771	-617.791012	48.7
$14^{2-}(t)$						
B3LYP/6-31G(d)	C_1	-617.	8882346	0.241607	-617.684378	88.0
B3LYP/6-31+G(d,p)	C_1	-617.	9804216	0.240607	-617.777831	57.0

Table S4 (continued).

Compd						
baisc set	Molecular point group		Е,	ZPE,	G,	ΔG,
			hartree	hartree	hartree	kcal ^a
15						
B3LYP/6-31G(d)	C_1	-656	.1807873	0.258797	-655.958264	(0)
B3LYP/6-31+G(d,p)	C_1	-656	.223446	0.257654	-656.002099	(0)
15²⁻ (s)						
B3LYP/6-31G(d)	C_1	-656	.0498283	0.248740	-655.837842	75.6
B3LYP/6-31+G(d,p)	C_1	-656	.13706	0.247232	-655.926797	47.3
15²⁻ (t)						
B3LYP/6-31G(d)	C_1	-656	.0312338	0.248408	-655.820504	86.4
B3LYP/6-31+G(d,p)	C_1	-656	.120833	0.247308	-655.911436	56.9

Table S4 (continued).