Focal Point Analysis of the Singlet-Triplet Energy Gap of Octacene and Larger Acenes

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Table S1: Focal point analysis of the vertical singlet-triplet gaps of benzene (all energies and corrections are given in kcal/mol). The Δ values are the singlet-triplet energy gaps at a given level. The +MP2, +MP3, +MP4, +CCSD, and +CCSD(T) entries correspond to the corrections obtained at the MP2, MP3, MP4, CCSD, and CCSD(T) levels, compared with the HF, MP2, MP3, MP4, and CCSD levels, respectively. "Well to well" S_0-T_1 excitation energies (WWE_{S-T}) results are in parenthesis

BENZENE										
	cc-pVDZ	cc-pVTZ	cc-pVQZ	cc-pV5Z	aug-cc-pVDZ	aug-cc-pVTZ	aug-cc-pVQZ	cc-pV∞Z	aug-cc-pV∞Z	cc-pV∞Z
# basis	114	264	510	876	192	414	756	(F/S-QZ)	(F/S-AQZ)	(F/S-5Z)
ΔHF	78.99	77.79	77.57	77.48	78.30	77.61	77.48	77.52[a]	77.46[b]	77.44[c]
	(63.13)	(63.09)	(63.06)	(63.07)	(–)	(–)	(–)	(63.04)[a]	(–)	(63.08)[c]
+MP2	46.84	48.08	48.51	48.62	46.86	47.83	48.39	48.82[d]	48.83[e]	48.68[f]
	(47.77)	(50.40)	(51.29)	(51.52)	(–)	(–)	(–)	(51.90)[d]	(–)	(51.68)[f]
+MP3	-12.60	-14.17	-14.65		-12.87	-14.25	-14.70	-14.97[g]	-15.01[h]	
	(-13.89)	(-15.38)	(-15.88)		(–)	(–)	(–)	(-16.21)[g]	(–)	
+MP4(SDQ)	-4.88	-5.37	-5.58		-5.51	-5.58	-5.66	-5.73[i]	-5.73[j]	
	(-4.72)	(-5.23)	(-5.46)		(–)	(–)	(–)	(-5.62)[i]	(–)	
+CCSD	-2.90	-1.87	-1.55		-2.43	-1.67	-1.46	-1.34[k]	-1.33[l]	
	(-2.79)	(-1.83)	(–)		(–)	(–)	(–)	(–)	(–)	
+CCSD(T)	0.01	0.36	0.40		0.16	0.38	0.40	0.42[m]	0.41[n]	
	(0.43)	(0.63)	(–)		(–)	(–)	(–)	(–)	(–)	
ΔCCSD(T)	105.45	104.82	104.70		104.50	104.32	104.46			
	(89.93)	(91.67)	(–)		(–)	(–)	(–)			

a) F-QZ; b) F-AQZ; c) F-5Z; d) S_{MP2}-QZ; e) S_{MP2}-AQZ; f) S_{MP2}-5Z; g) S_{MP3}-QZ; h) S_{MP3}-AQZ; i) $S_{MP4(SDQ)}$-QZ; j) $S_{MP4(sdq)}$-AQZ; k) S_{CCSD}-QZ; l) S_{CCSD}-AQZ; m) $S_{CCSD(T)}$-QZ; n) $S_{CCSD(T)}$-AQZ

Table S2: Focal point analysis of the vertical singlet-triplet gaps of naphthalene. "Well to well" S_0-T_1 excitation energies (WWE_{S-T}) results are in parenthesis (all results are given in kcal/mol).

NAPHTHALENE										
	cc-pVDZ	cc-pVTZ	cc-pVQZ	cc-pV5Z	aug-cc-pVDZ	aug-cc-pVTZ	aug-cc-pVQZ	cc-pV∞Z	aug-cc-pV∞Z	cc-pV∞Z
# basis	180	412	790	1350	302	644	1168	F/S-QZ	F/S-AQZ	F/S-5Z
ΔHF	69.27 (50.69)	68.18 (50.57)	67.88 (50.45)	67.71 (50.40)	68.13 (–)	67.74 (–)	67.67 (–)	67.76[a] (50.38)[a]	67.65[b] (–)	67.62[c] (50.38)[c]
+MP2	21.91 (32.04)	22.83 (34.04)	23.24 (34.72)	23.40 (34.92)	22.36 (–)	22.913 (–)	23.28 (–)	23.54[d] (35.18)[d]	23.56[e] (–)	23.56[f] (35.09)[f]
+MP3	-7.50 (-11.81)	-8.34 (-12.92)	-8.59 (-13.26)		-7.64 (–)	-8.35 (–)		-8.76[g] (-13.48)[g]		
+MP4(SDQ)	-3.97 (-4.64)	-4.25 (-5.04)	-4.36 (-5.21)		-4.25 (–)	-4.32 (–)		-4.44[h] (-5.33)[h]		
+CCSD	-0.03 (-0.55)	0.60 (0.19)			0.19 (–)					
+CCSD(T)	-2.66 (-1.12)	-2.56 (-1.02)			-2.56 (–)					
ΔCCSD(T)	77.03 (64.62)	76.46 (65.82)			76.22 (–)					

a) F-QZ; b) F-AQZ; c) F-5Z; d) S_{MP2}-QZ; e) S_{MP2}-AQZ; f) S_{MP2}-5Z; g) S_{MP3}-QZ; h) S_{MP4SDQ}-QZ

Table S3: Focal point analysis of the vertical singlet-triplet gaps of anthracene. "Well to well" S_0-T_1 excitation energies (WWE_{S-T}) results are in parenthesis (all results are given in kcal/mol).

ANTHRACENE										
	cc-pVDZ	cc-pVTZ	cc-pVQZ	cc-pV5Z	aug-cc-pVDZ	aug-cc-pVTZ	aug-cc-pVQZ	cc-pV∞Z	aug-cc-pV∞Z	cc-pV∞Z
# basis	246	560	1070	1824	412	874	1580	F/S-QZ	F/S-AQZ	F/S-5Z
ΔHF	44.68	44.02	43.83	43.74	44.05	43.79	43.73	43.76[a]	43.71[b]	43.70[c]
	(30.83)	(30.91)	(30.82)	(30.79)	(–)	(–)	(–)	(30.75)[a]	(–)	(30.77)[c]
+MP2	18.63	19.26	19.66	19.85	18.99	19.44	19.75	19.98[d]	20.00[e]	20.04[f]
	(25.67)	(27.26)	(27.89)	(28.14)	(–)	(–)	(–)	(28.35)[d]	(–)	(28.36)[f]
+MP3	-4.23	-5.02	-5.29		-4.54	-5.13		-5.53[g]		
	(-7.68)	(-8.74)	(-9.08)		(–)	(–)		(-9.31)[g]		
+MP4(SDQ)	-2.39	-2.56	-2.66		-2.64	-2.67		-2.74[h]		
	(-3.13)	(-3.44)	(-3.60)		(–)	(–)		(-3.72)[h]		
+CCSD	1.05	1.49			1.23					
	(0.89)	(1.42)			(–)					
+CCSD(T)	-0.33	-0.18			-0.36					
	(0.52)	(0.67)			(–)					
ΔCCSD(T)	57.40	57.00			56.73					
	(47.10)	(48.09)			(–)					

a) F-QZ; b) F-AQZ; c) F-5Z; d) S_{MP2}-QZ; e) S_{MP2}-AQZ; f) S_{MP2}-5Z; g) S_{MP3}-QZ; h) S_{MP4SDQ}-QZ

Table S4: Focal point analysis of the vertical singlet-triplet gaps of naphthacene. "Well to well" S_0-T_1 excitation energies (WWE_{S-T}) results are in parenthesis (all results are given in kcal/mol).

NAPHTHACENE						
	cc-pVDZ	cc-pVTZ	cc-pVQZ	cc-pV5Z	cc-pV∞Z	cc-pV∞Z
# basis	312	708	1350	2298	(F/S-QZ)	(F/S-5Z)
ΔHF	25.05 (13.09)	24.53 (13.20)	24.40 (13.15)	24.36 (13.12)	24.36[a] (13.09)[a]	24.33[b] (13.10)[b]
+MP2	29.35 (35.76)	30.30 (37.39)	30.79 (38.05)	30.99 (38.31)	31.16[c] (38.54)[c]	31.19[d] (38.56)[d]
+MP3	-7.74 (-10.32)	-8.96 (-11.81)			-9.63[e] (-12.59)[e]	
+MP4(SDQ)	-4.13 (-4.77)	-4.49 (-5.23)			-4.83[f] (-5.65)[f]	
+CCSD	-0.27 (-0.56)	0.31 (0.17)				
+CCSD(T)	-1.06 (-0.16)	-1.01 (-0.09)				
ΔCCSD(T)	41.19 (33.05)	40.67 (33.63)				

a) F-QZ; b) F-5Z; c) S_{MP2}-QZ; d) S_{MP2}-5Z; e) S_{MP3}-QZ; f) S_{MP4SDQ}-QZ

Table S5: Focal point analysis of the vertical singlet-triplet gaps of pentacene. "Well to well" S_0-T_1 excitation energies (WWE_{S-T}) results are in parenthesis (all results are given in kcal/mol).

PENTACENE				
	cc-pVDZ	cc-pVTZ	cc-pVQZ	cc-pV∞Z
# basis	378	856	1630	(F/S-QZ)
ΔHF	11.50 (0.46)	11.02 (0.49)	10.91 (0.44)	10.88[a] (0.39)[a]
+MP2	34.11 (42.53)	35.36 (44.40)	35.94 (45.13)	36.37[b] (45.66)[b]
+MP3	-9.07 (-12.44)	-10.54 (-14.28)		
+MP4(SDQ)	-4.83 (-5.96)	-5.34 (-6.60)		
+CCSD	0.08 (-0.69)			
+CCSD(T)	0.21 (1.06)			
ΔCCSD(T)	31.99 (24.95)			

a) F-QZ; b) S_{MP2}-QZ

Table S6: Focal point analysis of the vertical singlet-triplet gaps of hexacene. "Well to well" S_0-T_1 excitation energies (WWE_{S-T}) results are in parenthesis (all results are given in kcal/mol).

HEXACENE				
	cc-pVDZ	cc-pVTZ	cc-pVQZ	cc-pV∞Z
# basis	444	1004	1910	(F/S-QZ)
ΔHF	0.18 (-9.92)	-0.28 (-9.96)	-0.37 (-10.01)	-0.39[a] (-10.05)[a]
+MP2	40.59 (49.29)	42.08 (51.38)	42.74 (52.19)	43.22[b] (52.77)[b]
+MP3	-11.05 (14.55)	-12.78 (-16.69)		
+MP4(SDQ)	-5.69 (-6.90)	-6.35 (-7.72)		
+CCSD	-0.72 (-1.41)			
+CCSD(T)	0.23 (1.08)			
ΔCCSD(T)	23.53 (17.60)			

a) F-QZ; b) S_{MP2}-QZ

Table S7: Focal point analysis of the vertical singlet-triplet gaps of heptacene. "Well to well" S_0-T_1 excitation energies (WWE_{S-T}) results are in parenthesis (all results are given in kcal/mol).

HEPTACENE				
	cc-pVDZ	cc-pVTZ	cc-pVQZ	cc-pV∞Z
# basis	510	1152	2190	(F/S-QZ)
ΔHF	-8.69 (-18.39)	-9.17 (-18.54)	-9.26 (-18.60)	-9.28[a] (-18.63)[a]
+MP2	49.20 (58.50)	51.10 (60.93)	51.86 (61.83)	52.41[b] (62.47)[b]
+MP3	-14.04 (-17.70)	-16.15 (-20.26)		
+MP4(SDQ)	-7.37 (-8.62)	-8.25 (-9.65)		
+CCSD	-1.41 (-2.28)			
+CCSD(T)	1.16 (2.03)			
ΔCCSD(T)	18.86 (13.54)			

a) F-QZ; b) S_{MP2}-QZ