Supplementary material to: Thermally-assisted-occupation density functional theory with generalized-gradient approximations

Jeng-Da Chai*
Department of Physics, Center for Theoretical Sciences, and Center for Quantum Science and Engineering, National Taiwan University, Taipei 10617, Taiwan

* Electronic mail: jdchai@phys.ntu.edu.tw

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TABLES

TABLE S1. Non-hydrogen transfer barrier heights (in kcal/mol) of the NHTBH38/04 set [1].

			KS-DFT				TAO-DFT			
Reactions		ΔE_{ref}	LDA	PBE	BLYP	BLYP-D	LDA	PBE	BLYP	BLYP-D
Heavy-atom transfer reactions										
$H + N_2O \rightarrow OH + N_2$	V^f	18.14	2.69	9.97	8.54	8.19	2.63	9.92	8.48	8.13
	V^r	83.22	32.09	52.46	61.67	61.24	37.21	53.40	62.92	62.48
$H + FH \rightarrow HF + H$	V^f	42.18	18.48	27.07	26.03	25.76	18.57	27.14	26.10	25.83
	V^r	42.18	18.48	27.07	26.03	25.76	18.57	27.14	26.10	25.83
$H + ClH \rightarrow HCl + H$	V^f	18.00	2.27	9.64	9.80	9.74	2.14	9.51	9.66	9.60
	V^r	18.00	2.27	9.64	9.80	9.74	2.14	9.51	9.66	9.60
$H + FCH_3 \rightarrow HF + CH_3$	V^f	30.38	13.36	18.51	16.12	15.33	13.36	18.52	16.12	15.33
	V^r	57.02	31.72	41.00	42.27	41.33	31.62	40.88	42.14	41.21
$H + F_2 \rightarrow HF + F$	V^f	2.27	-15.97	-9.86	-11.66	-11.78	-16.13	-9.98	-11.79	-11.91
	V^r	106.18	69.40	80.86	82.15	82.02	77.32	82.70	84.15	84.03
$CH_3 + FCl \rightarrow CH_3F + Cl$	V^f	7.43	-11.50	-6.48	-6.97	-8.45	-11.93	-6.78	-7.30	-8.78
	V^r	60.17	37.67	41.63	41.76	40.43	46.51	47.37	48.19	46.85
Nucleophilic substitution reactions										
$F^- + CH_3F \rightarrow FCH_3 + F^-$	V^f	-0.34	-12.18	-8.31	-7.90	-8.95	-12.39	-8.51	-8.10	-9.15
	V^r	-0.34	-12.18	-8.31	-7.90	-8.95	-12.39	-8.51	-8.10	-9.15
$F^-\cdots CH_3F \rightarrow FCH_3\cdots F^-$	V^f	13.38	6.55	7.06	6.50	6.84	6.45	6.96	6.40	6.74
	V^r	13.38	6.55	7.06	6.50	6.84	6.45	6.96	6.40	6.74
$Cl^- + CH_3Cl \rightarrow ClCH_3 + Cl^-$	V^f	3.10	-6.74	-3.80	-3.95	-5.69	-7.07	-4.13	-4.30	-6.03
	V^r	3.10	-6.74	-3.80	-3.95	-5.69	-7.07	-4.13	-4.30	-6.03
$Cl^-\cdots CH_3Cl \rightarrow ClCH_3\cdots Cl^-$	V^f	13.61	6.74	7.15	5.72	5.55	6.66	7.07	5.65	5.48
	V^r	13.61	6.74	7.15	5.72	5.55	6.66	7.07	5.65	5.48
$F^- + CH_3Cl \rightarrow FCH_3 + Cl^-$	V^f	-12.54	-23.45	-19.52	-19.35	-20.67	-23.59	-19.65	-19.47	-20.79
	V^r	20.11	10.10	12.31	13.03	11.62	9.68	11.90	12.61	11.19
$F^-\cdots CH_3Cl \rightarrow FCH_3\cdots Cl^-$	V^f	2.89	-1.04	-0.67	-1.65	-1.54	-1.07	-0.70	-1.68	-1.57
	V^r	29.62	21.65	21.45	21.03	21.08	21.49	21.29	20.87	20.92
$OH^- + CH_3F \rightarrow HOCH_3 + F^-$	V^f	-2.78	-14.36	-10.59	-9.77	-11.56	-14.57	-10.74	-9.90	-11.69
	V^r	17.33	5.70	9.14	9.07	7.79	5.60	9.06	9.00	7.72
$OH^-\cdots CH_3F \rightarrow HOCH_3\cdots F^-$	V^f	10.96	3.39	3.88	3.73	3.17	3.27	3.85	3.73	3.17
	V^r	47.20	47.53	43.21	40.24	39.70	47.58	43.28	40.31	39.77
Unimolecular and association reactions										
$H + N_2 \rightarrow HN_2$	V^f	14.69	-2.19	5.19	5.24	5.08	-2.35	5.04	5.09	4.92
	V^r	10.72	9.44	9.08	8.51	8.38	9.60	9.19	8.61	8.48
$H + CO \rightarrow HCO$	V^f	3.17	-7.57	-1.69	-1.95	-2.25	-7.71	-1.83	-2.09	-2.39
	V^r	22.68	26.34	24.66	23.34	23.13	26.54	24.81	23.49	23.28
$H + C_2H_4 \rightarrow CH_3CH_2$	V^f	1.72	-5.34	-0.14	-0.69	-1.78	-5.46	-0.27	-0.81	-1.90
	V^r	41.75	39.21	40.20	38.11	37.63	39.37	40.35	38.27	37.78
$CH_3 + C_2H_4 \rightarrow CH_3CH_2CH_2$	V^f	6.85	-5.81	1.50	4.72	1.48	-6.13	1.18	4.39	1.15
	V^r	32.97	32.95	29.76	24.88	24.13	33.08	29.90	25.02	24.27
$HCN \rightarrow HNC$	V^f	48.16	44.83	45.60	46.76	46.94	44.89	45.66	46.81	46.99
	V^r	33.11	30.60	30.50	31.68	31.80	30.60	30.50	31.68	31.80
MSE			-12.41	-8.52	-8.69	-9.32	-11.93	-8.38	-8.52	-9.15
MAE			12.62	8.62	8.72	9.35	12.15	8.49	8.56	9.19
rms			16.13	10.61	10.27	10.83	15.09	10.28	9.90	10.46

Max(−)			-51.13	-30.76	-24.03	-24.16	-46.01	-29.82	-22.03	-22.15
Max(+)			3.66	1.98	0.66	0.45	3.86	2.13	0.81	0.60

TABLE S2. Hydrogen transfer barrier heights (in kcal/mol) of the HTBH38/04 set [1].

			KS-DFT				TAO-DFT			
Reactions		ΔE_{ref}	LDA	PBE	BLYP	BLYP-D	LDA	PBE	BLYP	BLYP-D
$H + HCl \rightarrow H_2 + Cl$	V^f	5.7	-3.14	0.56	-2.45	-2.58	-3.68	0.17	-2.89	-3.02
	V^r	8.7	-11.27	-1.95	1.84	1.71	-2.70	3.54	7.98	7.86
$OH + H_2 \rightarrow H + H_2O$	V^f	5.1	-18.39	-6.36	-3.49	-3.95	-13.65	-5.61	-2.43	-2.89
	V^r	21.2	11.33	13.69	10.39	9.96	10.88	13.44	10.13	9.70
$CH_3 + H_2 \rightarrow H + CH_4$	V^f	12.1	-5.35	3.82	7.14	5.96	-5.58	3.59	6.91	5.73
	V^r	15.3	4.94	9.32	7.65	6.61	4.87	9.24	7.58	6.54
$OH + CH_4 \rightarrow CH_3 + H_2O$	V^f	6.7	-17.22	-5.65	-2.75	-4.01	-12.41	-4.87	-1.64	-2.92
	V^r	19.6	2.21	8.91	10.63	9.24	1.68	8.52	10.24	8.86
$H + H_2 \rightarrow H_2 + H$	V^f	9.6	-2.70	3.64	2.86	2.67	-2.80	3.53	2.76	2.57
	V^r	9.6	-2.70	3.64	2.86	2.67	-2.80	3.53	2.76	2.57
$OH + NH_3 \rightarrow H_2O + NH_2$	V^f	3.2	-23.88	-11.94	-9.20	-10.46	-19.22	-11.26	-8.21	-9.47
	V^r	12.7	-10.71	-0.71	1.81	0.47	-11.30	-1.14	1.38	0.04
$HCl + CH_3 \rightarrow Cl + CH_4$	V^f	1.7	-13.74	-5.94	-3.51	-5.09	-14.16	-6.30	-3.88	-5.46
	V^r	7.9	-11.58	-2.95	1.29	-0.15	-2.73	2.73	7.66	6.22
$OH + C_2H_6 \rightarrow H_2O + C_2H_5$	V^f	3.4	-20.98	-9.03	-6.12	-7.54	-16.17	-8.26	-5.02	-6.45
	V^r	19.9	4.79	10.76	12.36	10.26	4.26	10.37	11.97	9.87
$F + H_2 \rightarrow HF + H$	V^f	1.8	-24.20	-12.97	-11.61	-11.86	-17.16	-11.52	-9.97	-10.22
	V^r	33.4	25.71	25.12	20.70	20.45	24.80	24.73	20.32	20.07
$O + CH_4 \rightarrow OH + CH_3$	V^f	13.7	-10.69	-0.79	1.44	0.52	-9.95	-1.14	1.20	-0.17
	V^r	8.1	-9.27	-0.57	1.68	0.61	-9.32	-0.68	1.50	0.46
$H + PH_3 \rightarrow PH_2 + H_2$	V^f	3.1	-7.35	-1.79	-2.63	-3.14	-7.46	-1.90	-2.73	-3.24
	V^r	23.2	9.24	17.91	21.58	20.38	9.02	17.68	21.34	20.15
$H + HO \rightarrow H_2 + O$	V^f	10.7	-1.69	3.75	1.60	1.48	-1.55	3.84	1.66	1.58
	V^r	13.1	-13.40	-1.98	0.86	0.74	-12.63	-2.27	0.69	0.13
$H + H_2S \rightarrow H_2 + HS$	V^f	3.5	-6.73	-1.22	-2.20	-2.59	-7.03	-1.42	-2.48	-2.86
	V^r	17.3	-0.86	9.10	14.00	13.36	4.93	12.53	18.07	17.43
$O + HCl \rightarrow OH + Cl$	V^f	9.8	-23.13	-10.54	-8.78	-8.86	-19.48	-10.85	-8.75	-9.32
	V^r	10.4	-19.55	-7.33	-3.75	-3.83	-7.42	-1.36	3.09	3.00
$NH_2 + CH_3 \rightarrow CH_4 + NH$	V^f	8.0	-8.37	0.71	3.57	1.82	-8.62	0.43	3.28	1.53
	V^r	22.4	2.16	10.56	13.31	11.66	1.93	10.34	13.09	11.44
$NH_2 + C_2H_5 \rightarrow C_2H_6 + NH$	V^f	7.5	-5.76	2.89	5.94	3.56	-6.02	2.60	5.64	3.26
	V^r	18.3	-1.57	7.51	10.59	8.87	-1.81	7.27	10.34	8.62
$C_2H_6 + NH_2 \rightarrow NH_3 + C_2H_5$	V^f	10.4	-9.69	1.44	5.25	3.08	-9.91	1.18	4.99	2.82
	V^r	17.4	2.91	9.99	12.72	9.94	2.60	9.68	12.40	9.62
$NH_2 + CH_4 \rightarrow CH_3 + NH_3$	V^f	14.5	-6.16	4.39	7.99	6.04	-6.37	4.15	7.75	5.80
	V^r	17.8	0.10	7.71	10.35	8.37	-0.20	7.41	10.05	8.06
s-trans cis-$C_5H_8 \rightarrow$ *s-trans cis*-C_5H_8	V^f	38.4	24.99	31.19	35.82	34.69	24.88	31.08	35.70	34.58
	V^r	38.4	24.99	31.19	35.82	34.69	24.88	31.08	35.70	34.58
MSE			-17.90	-9.67	-7.84	-8.89	-16.34	-9.20	-7.25	-8.33
MAE			17.90	9.67	7.84	8.89	16.34	9.20	7.29	8.34
rms			18.92	10.37	8.66	9.52	17.06	9.87	8.24	9.17
Max(−)			-32.93	-20.34	-18.58	-18.66	-29.28	-20.65	-18.55	-19.12
Max(+)			-7.69	-4.61	-1.56	-2.82	-8.60	-4.77	0.77	0.13

TABLE S3. Interaction energies (in kcal/mol) of the S22 set [2]. The counterpoise corrections are used to reduce the basis set superposition errors. Monomer deformation energies are not included.

		KS-DFT				TAO-DFT			
Complex [Symmetry]	ΔE_{ref}	LDA	PBE	BLYP	BLYP-D	LDA	PBE	BLYP	BLYP-D
Hydrogen bonded complexes									
$(NH_3)_2$ [C_{2h}]	-3.17	-5.10	-2.83	-1.78	-3.44	-5.27	-3.00	-1.96	-3.63
$(H_2O)_2$ [C_s]	-5.02	-7.78	-4.91	-3.99	-4.92	-7.95	-5.09	-4.18	-5.11
Formic acid dimer [C_{2h}]	-18.61	-26.82	-18.08	-15.48	-18.50	-27.22	-18.49	-15.89	-18.91
Formamide dimer [C_{2h}]	-15.96	-21.82	-14.69	-12.44	-15.63	-22.21	-15.08	-12.85	-16.03
Uracil dimer [C_{2h}]	-20.65	-26.15	-18.45	-16.21	-20.21	-26.51	-18.82	-16.59	-20.59
2-pyridoxine·2-aminopyridine [C_1]	-16.71	-22.77	-15.27	-12.51	-17.28	-23.18	-15.68	-12.94	-17.71
Adenine·thymine WC [C_1]	-16.37	-21.99	-14.28	-11.42	-16.50	-22.43	-14.73	-11.88	-16.96
MSE		-5.13	1.14	3.24	0.00	-5.47	0.80	2.89	-0.35
MAE		5.13	1.14	3.24	0.28	5.47	0.82	2.89	0.37
Dispersion complexes									
$(CH_4)_2$ [D_{3d}]	-0.53	-0.83	-0.08	0.68	-0.31	-0.95	-0.20	0.55	-0.44
$(C_2H_4)_2$ [D_{2d}]	-1.51	-2.49	-0.31	1.12	-1.44	-2.71	-0.54	0.89	-1.68
Benzene·CH_4 [C_3]	-1.50	-2.01	-0.01	1.39	-1.23	-2.21	-0.22	1.17	-1.45
Benzene dimer [C_{2h}]	-2.73	-2.62	1.90	4.94	-1.93	-3.03	1.49	4.50	-2.36
Pyrazine dimer [C_s]	-4.42	-4.46	0.73	3.80	-3.65	-4.86	0.32	3.36	-4.09
Uracil dimer [C_2]	-10.12	-10.15	-2.69	1.13	-9.68	-10.66	-3.21	0.58	-10.24
Indole·benzene [C_1]	-5.22	-4.38	2.24	6.32	-3.92	-4.90	1.71	5.76	-4.47
Adenine·thymine stack [C_1]	-12.23	-11.96	-1.33	4.06	-11.81	-12.63	-2.01	3.35	-12.52
MSE		-0.08	4.84	7.71	0.54	-0.46	4.45	7.30	0.13
MAE		0.38	4.84	7.71	0.54	0.54	4.45	7.30	0.27
Mixed complexes									
Ethene·ethine [C_{2v}]	-1.53	-2.27	-1.16	-0.29	-1.49	-2.41	-1.30	-0.45	-1.64
Benzene·H_2O [C_s]	-3.28	-4.44	-2.04	-0.49	-3.29	-4.67	-2.27	-0.74	-3.54
Benzene·NH_3 [C_s]	-2.35	-3.03	-0.92	0.55	-2.18	-3.24	-1.14	0.31	-2.42
Benzene·HCN [C_s]	-4.46	-5.85	-2.81	-0.94	-4.65	-6.09	-3.05	-1.19	-4.91
Benzene dimer [C_{2v}]	-2.74	-3.06	-0.10	1.86	-2.51	-3.33	-0.38	1.57	-2.81
Indole·benzene T-shape [C_1]	-5.73	-6.26	-2.02	0.69	-5.67	-6.63	-2.39	0.30	-6.05
Phenol dimer [C_1]	-7.05	-9.01	-3.86	-1.75	-6.65	-9.34	-4.20	-2.10	-7.00
MSE		-0.97	2.03	3.83	0.10	-1.22	1.77	3.55	-0.18
MAE		0.97	2.03	3.83	0.16	1.22	1.77	3.55	0.19
MSE		-1.97	2.77	5.05	0.23	-2.30	2.44	4.70	-0.12
MAE		2.08	2.77	5.05	0.33	2.33	2.44	4.70	0.28
rms		3.18	3.89	6.31	0.45	3.40	3.57	5.95	0.37
Max(−)		-8.21	0.11	1.03	-0.57	-8.61	-0.07	0.84	-1.00
Max(+)		0.84	10.90	16.29	1.30	0.32	10.22	15.58	0.75

TABLE S4. Comparison of errors (in kcal/mol) of the reaction energies (in kcal/mol) of the 30 chemical reactions in the NHTBH38/04 and HTBH38/04 sets [1].

		KS-DFT				TAO-DFT			
Reactions	ΔE_{ref}	LDA	PBE	BLYP	BLYP-D	LDA	PBE	BLYP	BLYP-D
$H + N_2O \rightarrow OH + N_2$	-65.08	35.68	22.59	11.96	12.03	30.50	21.60	10.65	10.73
$H + FCH_3 \rightarrow HF + CH_3$	-26.64	8.28	4.16	0.49	0.63	8.39	4.28	0.62	0.77
$H + F_2 \rightarrow HF + F$	-103.91	18.54	13.19	10.10	10.10	10.46	11.23	7.97	7.97
$CH_3 + FCl \rightarrow CH_3F + Cl$	-52.74	3.57	4.64	4.01	3.86	-5.71	-1.41	-2.75	-2.89
$F^- + CH_3Cl \rightarrow FCH_3 + Cl^-$	-32.65	-0.90	0.82	0.27	0.37	-0.62	1.11	0.57	0.67

$F^-\cdots CH_3Cl \rightarrow FCH_3\cdots Cl^-$	-26.73	4.05	4.61	4.05	4.11	4.18	4.73	4.17	4.24
$OH^- + CH_3F \rightarrow HOCH_3 + F^-$	-20.11	0.05	0.38	1.27	0.75	-0.07	0.30	1.21	0.70
$OH^-\cdots CH_3F \rightarrow HOCH_3\cdots F^-$	-36.24	-7.90	-3.09	-0.27	-0.29	-8.07	-3.19	-0.34	-0.36
$H + N_2 \rightarrow HN_2$	3.97	-15.60	-7.86	-7.24	-7.28	-15.92	-8.12	-7.49	-7.53
$H + CO \rightarrow HCO$	-19.51	-14.40	-6.84	-5.78	-5.87	-14.74	-7.13	-6.07	-6.16
$H + C_2H_4 \rightarrow CH_3CH_2$	-40.03	-4.52	-0.31	1.22	0.62	-4.79	-0.59	0.95	0.34
$CH_3 + C_2H_4 \rightarrow CH_3CH_2CH_2$	-26.12	-12.64	-2.14	5.96	3.47	-13.09	-2.60	5.49	2.99
$HCN \rightarrow HNC$	15.05	-0.83	0.06	0.02	0.09	-0.77	0.12	0.08	0.14
$H + HCl \rightarrow H_2 + Cl$	-3.0	11.13	5.51	-1.29	-1.29	2.01	-0.37	-7.87	-7.87
$OH + H_2 \rightarrow H + H_2O$	-16.1	-13.62	-3.95	2.22	2.19	-8.43	-2.95	3.55	3.51
$CH_3 + H_2 \rightarrow H + CH_4$	-3.2	-7.09	-2.30	2.70	2.55	-7.25	-2.45	2.53	2.39
$OH + CH_4 \rightarrow CH_3 + H_2O$	-12.9	-6.53	-1.65	-0.48	-0.36	-1.19	-0.49	1.02	1.13
$OH + NH_3 \rightarrow H_2O + NH_2$	-9.5	-3.67	-1.73	-1.51	-1.43	1.58	-0.63	-0.08	-0.01
$HCl + CH_3 \rightarrow Cl + CH_4$	-6.2	4.04	3.21	1.41	1.26	-5.23	-2.83	-5.34	-5.48
$OH + C_2H_6 \rightarrow H_2O + C_2H_5$	-16.5	-9.27	-3.29	-1.97	-1.30	-3.93	-2.13	-0.49	0.19
$F + H_2 \rightarrow HF + H$	-31.6	-18.31	-6.49	-0.72	-0.72	-10.36	-4.65	1.30	1.30
$O + CH_4 \rightarrow OH + CH_3$	5.6	-7.02	-5.83	-5.84	-5.69	-6.23	-6.06	-5.90	-6.23
$H + PH_3 \rightarrow PH_2 + H_2$	-20.1	3.51	0.40	-4.10	-3.42	3.63	0.52	-3.98	-3.29
$H + HO \rightarrow H_2 + O$	-2.4	14.11	8.12	3.14	3.14	13.48	8.52	3.37	3.84
$H + H_2S \rightarrow H_2 + HS$	-13.8	7.93	3.48	-2.41	-2.15	1.84	-0.15	-6.74	-6.49
$O + HCl \rightarrow OH + Cl$	-0.6	-2.98	-2.61	-4.43	-4.43	-11.46	-8.89	-11.24	-11.71
$NH_2 + CH_3 \rightarrow CH_4 + NH$	-14.4	3.87	4.55	4.66	4.56	3.85	4.49	4.59	4.49
$NH_2 + C_2H_5 \rightarrow C_2H_6 + NH$	-10.8	6.62	6.19	6.15	5.49	6.59	6.13	6.09	5.43
$C_2H_6 + NH_2 \rightarrow NH_3 + C_2H_5$	-7.0	-5.61	-1.55	-0.46	0.14	-5.51	-1.50	-0.40	0.20
$NH_2 + CH_4 \rightarrow CH_3 + NH_3$	-3.3	-2.96	-0.02	0.94	0.97	-2.87	0.03	1.00	1.04
MSE		-0.41	1.08	0.80	0.74	-1.32	0.23	-0.12	-0.20
MAE		8.51	4.39	3.23	3.02	7.09	3.97	3.80	3.67
rms		11.10	6.24	4.37	4.20	9.38	5.97	4.95	4.89
Max(−)		-18.31	-7.86	-7.24	-7.28	-15.92	-8.89	-11.24	-11.71
Max(+)		35.68	22.59	11.96	12.03	30.50	21.60	10.65	10.73

TABLE S5. The 166 experimentally determined equilibrium bond lengths (in Å) of 136 molecules included in EXTS [3]. Optimized bond lengths are calculated by various methods.

		KS-DFT				TAO-DFT			
Molecule	Experiment	LDA	PBE	BLYP	BLYP-D	LDA	PBE	BLYP	BLYP-D
H_2N^-	1.028	1.037	1.038	1.038	1.038	1.037	1.037	1.038	1.038
NO^- ($^3\Sigma^-$)	1.258	1.250	1.267	1.279	1.279	1.250	1.267	1.278	1.278
PO^- ($^3\Sigma^-$)	1.540	1.539	1.556	1.563	1.563	1.539	1.556	1.563	1.563
BeH^+ ($^1\Sigma^+$)	1.312	1.337	1.330	1.323	1.323	1.336	1.329	1.322	1.322
CH^+ ($^1\Sigma^+$)	1.131	1.162	1.153	1.147	1.147	1.162	1.153	1.147	1.147
CN^+ ($^1\Sigma^+$)	1.173	1.173	1.181	1.183	1.183	1.203	1.216	1.220	1.220
H_3^+	0.877	0.906	0.889	0.886	0.886	0.906	0.888	0.885	0.885
H_3O^+	0.976	0.990	0.988	0.989	0.990	0.990	0.987	0.989	0.990
HCO^+	1.097 (CH)	1.111	1.104	1.101	1.102	1.111	1.103	1.101	1.102
	1.105 (CO)	1.105	1.113	1.113	1.113	1.105	1.113	1.113	1.113
MgH^+ ($^1\Sigma^+$)	1.652	1.671	1.673	1.669	1.670	1.669	1.671	1.668	1.669
NO^+ ($^1\Sigma^+$)	1.063	1.062	1.070	1.071	1.071	1.062	1.069	1.071	1.071
NS^+ ($^1\Sigma^+$)	1.440	1.433	1.444	1.447	1.447	1.433	1.444	1.446	1.446
OH^+ ($^3\Sigma^-$)	1.029	1.055	1.047	1.050	1.050	1.055	1.046	1.050	1.050
SiH^+ ($^1\Sigma^+$)	1.504	1.538	1.532	1.527	1.527	1.537	1.532	1.526	1.526

NH_4^+	1.021	1.035	1.031	1.032	1.033	1.034	1.031	1.031	1.032
AlCl ($^1\Sigma^+$)	2.130	2.136	2.162	2.178	2.179	2.135	2.161	2.178	2.178
AlF ($^1\Sigma^+$)	1.654	1.669	1.693	1.698	1.698	1.669	1.692	1.698	1.698
AlH ($^1\Sigma^+$)	1.648	1.680	1.679	1.674	1.674	1.679	1.678	1.673	1.673
AlN ($^3\Pi_i$)	1.786	1.769	1.792	1.799	1.799	1.774	1.799	1.810	1.811
BCl ($^1\Sigma^+$)	1.797	1.706	1.729	1.734	1.734	1.706	1.728	1.733	1.733
BeO ($^1\Sigma^+$)	1.331	1.326	1.338	1.339	1.339	1.331	1.345	1.347	1.347
BeS ($^1\Sigma^+$)	1.742	1.739	1.751	1.754	1.754	1.753	1.768	1.775	1.775
BF ($^1\Sigma^+$)	1.263	1.256	1.271	1.272	1.272	1.256	1.271	1.272	1.272
BF_3	1.307	1.307	1.322	1.325	1.326	1.307	1.322	1.325	1.326
BH ($^1\Sigma^+$)	1.232	1.256	1.251	1.240	1.240	1.254	1.250	1.239	1.239
BN ($^3\Pi$)	1.281	1.323	1.332	1.333	1.333	1.322	1.331	1.332	1.332
C_6H_6	1.390 (CC)	1.385	1.397	1.401	1.402	1.385	1.397	1.400	1.402
	1.086 (CH)	1.094	1.091	1.088	1.089	1.093	1.091	1.088	1.088
CCl_2O	1.177 (CO)	1.177	1.185	1.184	1.184	1.177	1.185	1.184	1.184
	1.737 (CCl)	1.731	1.754	1.777	1.780	1.730	1.754	1.776	1.779
CF_4	1.315	1.318	1.335	1.343	1.344	1.317	1.335	1.343	1.344
CH_2Cl_2	1.766 (CCl)	1.754	1.779	1.801	1.805	1.754	1.778	1.800	1.804
	1.080 (CH)	1.096	1.092	1.088	1.090	1.095	1.091	1.088	1.089
CH_2F_2	1.351 (CF)	1.348	1.369	1.380	1.382	1.348	1.369	1.380	1.382
	1.084 (CH)	1.105	1.100	1.096	1.099	1.105	1.100	1.096	1.098
CH_2O_2 (*trans*)	1.201 (C=O)	1.198	1.207	1.208	1.208	1.198	1.206	1.208	1.208
	1.091 (CH)	1.111	1.106	1.103	1.104	1.110	1.106	1.103	1.103
	1.340 (CO)	1.332	1.353	1.362	1.363	1.332	1.353	1.362	1.363
	0.969 (OH)	0.983	0.980	0.981	0.981	0.983	0.979	0.980	0.980
CH_3Cl	1.086 (CH)	1.096	1.094	1.091	1.093	1.096	1.093	1.090	1.093
	1.778 (CCl)	1.763	1.789	1.815	1.820	1.762	1.788	1.815	1.819
CH_3F	1.086 (CH)	1.102	1.099	1.096	1.098	1.102	1.098	1.095	1.098
	1.383 (CF)	1.371	1.395	1.409	1.412	1.371	1.395	1.409	1.412
CH_4	1.087	1.097	1.096	1.094	1.097	1.097	1.095	1.094	1.096
CHF_3	1.328 (CF)	1.330	1.349	1.358	1.359	1.330	1.349	1.357	1.359
	1.091 (CH)	1.105	1.100	1.096	1.097	1.105	1.099	1.095	1.097
Cl_2 ($^1\Sigma_g^+$)	1.988	1.980	2.005	2.040	2.040	1.979	2.005	2.040	2.040
ClCN	1.629 (CCl)	1.612	1.630	1.642	1.643	1.612	1.629	1.642	1.643
	1.160 (CN)	1.160	1.167	1.166	1.167	1.160	1.167	1.166	1.167
ClF	1.628	1.625	1.653	1.674	1.675	1.625	1.653	1.674	1.674
CO ($^1\Sigma^+$)	1.128	1.127	1.136	1.136	1.136	1.127	1.136	1.136	1.136
CO_2	1.160	1.162	1.171	1.172	1.172	1.161	1.170	1.172	1.172
CS ($^1\Sigma^+$)	1.535	1.533	1.546	1.548	1.548	1.533	1.546	1.548	1.548
CS_2	1.553	1.551	1.562	1.567	1.568	1.550	1.562	1.567	1.568
F_2 ($^1\Sigma_g^+$)	1.412	1.383	1.412	1.431	1.431	1.383	1.411	1.431	1.431
F_2O	1.405	1.388	1.417	1.437	1.438	1.388	1.417	1.437	1.438
F_2S	1.587	1.598	1.624	1.638	1.639	1.598	1.623	1.638	1.639
F_2Si	1.590	1.607	1.629	1.635	1.636	1.607	1.629	1.635	1.636
F_3HSi	1.562 (SiF)	1.575	1.595	1.599	1.600	1.575	1.594	1.599	1.600
	1.447 (SiH)	1.470	1.468	1.463	1.460	1.469	1.468	1.462	1.460
H_2 ($^1\Sigma_g^+$)	0.741	0.766	0.751	0.747	0.747	0.766	0.750	0.746	0.746
H_2CCCH_2	1.076 (CH)	1.095	1.092	1.090	1.091	1.094	1.091	1.089	1.091
	1.308 (CC)	1.298	1.308	1.308	1.309	1.298	1.307	1.308	1.309
H_2CS	1.611 (CS)	1.601	1.614	1.621	1.622	1.601	1.615	1.622	1.623
	1.086 (CH)	1.100	1.097	1.094	1.096	1.100	1.097	1.094	1.096
H_2O	0.958	0.971	0.969	0.971	0.971	0.970	0.969	0.971	0.971

H_2S	1.336	1.354	1.352	1.352	1.353	1.353	1.351	1.352	1.352
H_2Si	1.514	1.538	1.538	1.534	1.533	1.537	1.537	1.533	1.532
HCCCN	1.062 (CH)	1.075	1.071	1.068	1.068	1.075	1.071	1.067	1.068
	1.206 (C≡C)	1.208	1.214	1.212	1.213	1.208	1.214	1.212	1.213
	1.376 (CC)	1.355	1.366	1.367	1.368	1.355	1.365	1.367	1.368
	1.161 (C≡N)	1.162	1.170	1.169	1.169	1.162	1.170	1.169	1.169
HCCH	1.061 (CH)	1.074	1.070	1.067	1.068	1.074	1.070	1.067	1.068
	1.203 (CC)	1.202	1.207	1.206	1.207	1.201	1.207	1.206	1.206
HCl ($^1\Sigma^+$)	1.275	1.291	1.288	1.291	1.291	1.291	1.288	1.290	1.290
HCN	1.065 (CH)	1.079	1.075	1.072	1.073	1.079	1.075	1.072	1.073
	1.153 (CN)	1.151	1.158	1.157	1.158	1.151	1.158	1.157	1.157
HCP	1.066 (CH)	1.083	1.080	1.077	1.078	1.083	1.080	1.076	1.077
	1.540 (CP)	1.537	1.547	1.548	1.549	1.536	1.546	1.548	1.548
HF ($^1\Sigma^+$)	0.917	0.932	0.930	0.933	0.933	0.931	0.930	0.933	0.933
HNC	0.994 (NH)	1.009	1.006	1.005	1.006	1.009	1.005	1.005	1.005
	1.169 (NC)	1.168	1.176	1.175	1.175	1.167	1.176	1.175	1.175
HOCl	0.964 (OH)	0.978	0.976	0.978	0.978	0.977	0.976	0.977	0.978
	1.689 (OCl)	1.678	1.710	1.736	1.736	1.678	1.709	1.736	1.736
LiCl ($^1\Sigma^+$)	2.021	2.004	2.025	2.031	2.041	2.003	2.024	2.030	2.039
LiF ($^1\Sigma^+$)	1.564	1.560	1.583	1.584	1.586	1.559	1.582	1.583	1.586
LiH ($^1\Sigma^+$)	1.596	1.603	1.603	1.595	1.630	1.600	1.600	1.593	1.626
MgO ($^1\Sigma^+$)	1.749	1.726	1.751	1.757	1.757	1.754	1.782	1.789	1.789
MgS ($^1\Sigma^+$)	2.143	2.130	2.155	2.168	2.168	2.170	2.200	2.219	2.220
N_2 ($^1\Sigma_g^+$)	1.098	1.095	1.103	1.103	1.103	1.095	1.103	1.103	1.103
N_2O	1.127 (NN)	1.130	1.138	1.139	1.139	1.130	1.138	1.139	1.139
	1.185 (NO)	1.175	1.188	1.197	1.197	1.175	1.188	1.197	1.197
NaCl ($^1\Sigma^+$)	2.361	2.335	2.376	2.387	2.401	2.334	2.374	2.385	2.400
NaF ($^1\Sigma^+$)	1.926	1.908	1.947	1.951	1.956	1.907	1.946	1.950	1.955
NaH ($^1\Sigma^+$)	1.887	1.867	1.890	1.884	1.912	1.865	1.887	1.882	1.909
NF ($^3\Sigma^-$)	1.317	1.302	1.325	1.341	1.341	1.302	1.325	1.341	1.341
NH ($^3\Sigma^-$)	1.036	1.054	1.050	1.051	1.051	1.054	1.049	1.050	1.050
NH_3	1.012	1.007	1.004	1.005	1.006	1.007	1.004	1.004	1.005
O_2 ($^3\Sigma_g^-$)	1.208	1.203	1.217	1.228	1.228	1.203	1.217	1.228	1.228
O_3	1.272	1.250	1.270	1.286	1.286	1.251	1.271	1.287	1.287
OCS	1.147 (CO)	1.160	1.168	1.170	1.170	1.160	1.168	1.170	1.170
	1.561 (CS)	1.556	1.568	1.574	1.574	1.555	1.568	1.573	1.574
P_2 ($^1\Sigma_g^+$)	1.893	1.890	1.904	1.911	1.911	1.890	1.903	1.910	1.910
PF ($^3\Sigma^-$)	1.590	1.600	1.623	1.633	1.633	1.600	1.623	1.633	1.633
PH ($^3\Sigma^-$)	1.422	1.442	1.440	1.439	1.439	1.441	1.439	1.438	1.438
PH_3	1.413	1.431	1.430	1.428	1.429	1.431	1.430	1.428	1.428
PN ($^1\Sigma^+$)	1.491	1.486	1.498	1.500	1.500	1.486	1.498	1.499	1.499
S_2 ($^3\Sigma_g^-$)	1.889	1.896	1.911	1.929	1.929	1.895	1.910	1.928	1.928
S_2O	1.884 (SS)	1.889	1.908	1.925	1.926	1.889	1.908	1.926	1.927
	1.456 (SO)	1.463	1.478	1.485	1.486	1.463	1.478	1.485	1.486
SCS	1.553	1.551	1.562	1.567	1.568	1.550	1.562	1.567	1.568
SiO ($^1\Sigma^+$)	1.510	1.515	1.529	1.531	1.531	1.514	1.528	1.531	1.531
SiS ($^1\Sigma^+$)	1.929	1.936	1.952	1.960	1.960	1.935	1.951	1.959	1.959
SO ($^3\Sigma^-$)	1.481	1.489	1.504	1.513	1.513	1.489	1.503	1.513	1.513
SO_2	1.431	1.440	1.455	1.461	1.461	1.440	1.455	1.461	1.461
B_2H_6	1.314 (BH ×2)	1.312	1.319	1.317	1.321	1.311	1.319	1.317	1.320
	1.184 (BH ×4)	1.198	1.196	1.190	1.191	1.198	1.195	1.190	1.191
cyclopropane	1.501 (CC)	1.492	1.509	1.517	1.520	1.492	1.508	1.516	1.520

	1.083 (CH)	1.091	1.089	1.087	1.089	1.091	1.089	1.087	1.088
C_2^- ($^2\Sigma_g^+$)	1.268	1.258	1.269	1.268	1.268	1.265	1.274	1.275	1.275
NH^- ($^2\Pi_i$)	1.047	1.051	1.051	1.052	1.052	1.051	1.051	1.051	1.051
AlH^+ ($^2\Sigma^+$)	1.602	1.642	1.635	1.638	1.639	1.640	1.634	1.637	1.637
Cl_2^+ ($^2\Pi_{3/2g}$)	1.892	1.893	1.913	1.941	1.941	1.892	1.913	1.941	1.941
CO^+ ($^2\Sigma^+$)	1.115	1.114	1.122	1.123	1.123	1.114	1.121	1.123	1.123
HCl^+ ($^2\Pi_i$)	1.315	1.339	1.332	1.334	1.334	1.339	1.332	1.334	1.334
He_2^+ ($^2\Sigma_u^+$)	1.081	1.161	1.176	1.183	1.184	1.161	1.175	1.183	1.183
HF^+ ($^2\Pi_i$)	1.001	1.028	1.021	1.026	1.026	1.028	1.021	1.026	1.026
N_2^+ ($^2\Sigma_g^+$)	1.116	1.107	1.115	1.116	1.116	1.108	1.115	1.117	1.117
NH^+ ($^2\Pi_r$)	1.070	1.098	1.090	1.090	1.090	1.098	1.091	1.090	1.090
NH_3^+	1.014	1.037	1.032	1.032	1.034	1.037	1.032	1.032	1.033
O_2^+ ($^2\Pi_g$)	1.116	1.110	1.121	1.127	1.127	1.110	1.121	1.127	1.127
PF^+ ($^2\Pi_r$)	1.500	1.517	1.535	1.541	1.541	1.517	1.535	1.541	1.541
H_2O^+ ($^2B_1$)	0.999	1.019	1.014	1.017	1.017	1.019	1.014	1.016	1.017
AlS ($^2\Sigma^+$)	2.029	2.031	2.049	2.064	2.064	2.052	2.067	2.095	2.096
BeCl ($^2\Sigma^+$)	1.797	1.789	1.806	1.811	1.811	1.788	1.806	1.811	1.811
BeF ($^2\Sigma^+$)	1.361	1.358	1.374	1.376	1.376	1.358	1.373	1.375	1.375
BeH ($^2\Sigma^+$)	1.343	1.361	1.356	1.346	1.346	1.359	1.354	1.345	1.345
BO ($^2\Sigma^+$)	1.205	1.204	1.213	1.213	1.213	1.203	1.212	1.213	1.213
BS ($^2\Sigma^+$)	1.609	1.609	1.620	1.623	1.623	1.609	1.620	1.623	1.623
CCl ($^2\Pi_{1/2}$, $^2\Pi_{3/2}$)	1.645	1.632	1.657	1.672	1.672	1.630	1.654	1.668	1.668
CF ($^2\Pi_r$)	1.272	1.263	1.283	1.291	1.291	1.262	1.282	1.289	1.289
CH ($^2\Pi_r$)	1.120	1.139	1.136	1.132	1.132	1.139	1.135	1.131	1.131
CH_3	1.076	1.089	1.086	1.084	1.086	1.089	1.086	1.084	1.086
ClO ($^2\Pi_i$)	1.570	1.553	1.580	1.600	1.600	1.552	1.576	1.596	1.596
CN ($^2\Sigma^+$)	1.172	1.166	1.174	1.175	1.175	1.168	1.175	1.176	1.176
CP ($^2\Sigma^+$)	1.562	1.555	1.566	1.569	1.569	1.562	1.569	1.576	1.576
H_2N ($^2B_1$)	1.025	1.039	1.037	1.037	1.037	1.038	1.036	1.037	1.037
HO	0.970	0.986	0.983	0.985	0.985	0.985	0.983	0.985	0.985
HOO	0.971 (OH)	0.991	0.987	0.988	0.988	0.991	0.987	0.988	0.988
	1.331 (OO)	1.308	1.333	1.353	1.353	1.311	1.334	1.353	1.353
MgCl ($^2\Sigma^+$)	2.199	2.196	2.225	2.239	2.240	2.195	2.223	2.238	2.239
MgF ($^2\Sigma^+$)	1.750	1.756	1.783	1.788	1.789	1.755	1.782	1.788	1.788
MgH ($^2\Sigma^+$)	1.730	1.753	1.756	1.756	1.757	1.750	1.754	1.754	1.755
NO ($^2\Pi_r$)	1.151	1.146	1.157	1.161	1.161	1.146	1.157	1.161	1.161
NO_2 ($^2A_1$)	1.195	1.189	1.203	1.210	1.210	1.189	1.203	1.210	1.210
NS ($^2\Pi_r$)	1.494	1.491	1.505	1.510	1.510	1.491	1.505	1.510	1.510
OP ($^2\Pi_r$)	1.474	1.481	1.494	1.498	1.498	1.481	1.495	1.499	1.499
SF ($^2\Pi_{3/2}$, $^2\Pi_{1/2}$)	1.601	1.601	1.626	1.642	1.642	1.601	1.626	1.641	1.641
SH ($^2\Pi_i$)	1.345	1.359	1.356	1.357	1.357	1.358	1.356	1.356	1.356
SiCl ($^2\Pi_r$)	2.058	2.058	2.084	2.104	2.104	2.057	2.082	2.102	2.102
SiF ($^2\Pi_r$)	1.601	1.617	1.640	1.646	1.646	1.617	1.639	1.646	1.646
SiH ($^2\Pi_r$)	1.520	1.545	1.544	1.540	1.540	1.544	1.544	1.539	1.539
SiN ($^2\Sigma^+$)	1.572	1.564	1.578	1.582	1.582	1.586	1.597	1.607	1.607
HCO	1.119 (CH)	1.138	1.134	1.133	1.134	1.137	1.134	1.132	1.133
	1.175 (CO)	1.172	1.181	1.183	1.184	1.172	1.181	1.183	1.184
MSE		0.004	0.014	0.018	0.019	0.005	0.014	0.019	0.020
MAE		0.013	0.015	0.019	0.020	0.013	0.015	0.020	0.021
rms		0.017	0.019	0.024	0.025	0.017	0.020	0.025	0.026
Max(−)		-0.091	-0.069	-0.064	-0.063	-0.091	-0.069	-0.064	-0.064
Max(+)		0.081	0.095	0.103	0.103	0.080	0.095	0.102	0.102

TABLE S6. Singlet-triplet energy gap [$E_T - E_S$] (in kcal/mol), as a function of the acene length, calculated by various functionals in spin-unrestricted KS-DFT and TAO-DFT. The experimental data (uncorrected for zero-point vibrations, thermal vibrations, etc.) are taken from Refs. [4–7], the DMRG data are taken from Ref. [8], and the CCSD(T)/CBS data are taken from Ref. [9].

					KS-DFT				TAO-DFT			
n-acene	Experiment	DMRG/cc-pVDZ	DMRG/STO-3G	CCSD(T)/CBS	LDA	PBE	BLYP	BLYP-D	LDA	PBE	BLYP	BLYP-D
2	61.0	61.0	61.5	65.83	65.19	60.88	60.44	60.30	64.77	60.59	60.14	59.99
3	43.1	44.0	45.9	48.21	43.40	40.26	40.19	40.20	43.22	40.12	40.03	40.04
4	29.3	31.9	34.7	33.49	29.06	26.61	26.74	26.82	29.01	26.60	26.71	26.79
5	19.8	23.4	26.7	25.27	19.20	17.20	17.45	17.58	19.60	17.62	17.83	17.95
6		17.5	21.0	17.71	12.16	10.48	10.81	10.95	13.55	11.84	12.11	12.22
8			14.2	9.20	3.07	1.81	2.87	2.37	7.85	6.41	6.65	6.72
10			11.6	4.64	0.53	1.43	1.31	1.31	5.91	4.66	4.82	4.86
12			10.7		1.59	2.17	1.95	1.89	4.82	3.77	3.88	3.91
14					3.47	1.57	3.27	3.18	3.98	3.09	3.19	3.21
16					4.43	2.10	3.86	3.83	3.37	2.60	2.68	2.69
18									2.94	2.29	2.32	2.33
20									2.62	2.00	2.06	2.07
22									2.37	1.80	1.85	1.86
24									2.15	1.64	1.69	1.70
26									1.98	1.51	1.55	1.56
28									1.83	1.39	1.43	1.44
30									1.70	1.29	1.33	1.33
32									1.59	1.21	1.24	1.25
34									1.49	1.13	1.16	1.16
36									1.40	1.07	1.10	1.10
38									1.33	1.01	1.04	1.04
40									1.26	0.95	0.98	0.99
42									1.20	0.91	0.93	0.93
44									1.14	0.86	0.88	0.89
46									1.09	0.83	0.85	0.85
48									1.04	0.79	0.81	0.82
50									1.00	0.76	0.78	0.78
52									0.96	0.73	0.75	0.75
54									0.92	0.70	0.72	0.72
56									0.89	0.66	0.69	0.70
58									0.86	0.65	0.67	0.66
60									0.83	0.63	0.64	0.65
62									0.80	0.61	0.63	0.63
64									0.78	0.59	0.61	0.61
66									0.75	0.57	0.59	0.59
68									0.73	0.55	0.56	0.56
70									0.71	0.54	0.55	0.55
72									0.69	0.52	0.54	0.54
74									0.67	0.51	0.52	0.53
76									0.65	0.50	0.51	0.51
78									0.64	0.48	0.50	0.50
80									0.62	0.46	0.47	0.48
82									0.60	0.46	0.47	0.47
84									0.59	0.45	0.46	0.46
86									0.58	0.44	0.45	0.45
88									0.56	0.42	0.44	0.44
90									0.55	0.41	0.43	0.43
92									0.54	0.41	0.41	0.41
94									0.53	0.40	0.41	0.41

96	0.51	0.39	0.40	0.40
98	0.50	0.38	0.39	0.39
100	0.49	0.38	0.38	0.39

TABLE S7. Vertical ionization potential (in eV) for the lowest singlet state of n-acene as a function of the acene length, calculated by various functionals in spin-unrestricted TAO-DFT. The experimental data are taken from the compilation in Ref. [10], and the CCSD(T)/CBS data are taken from Ref. [11].

			TAO-DFT			
n-acene	Experiment	CCSD(T)/CBS	LDA	PBE	BLYP	BLYP-D
2	8.14	8.24	7.81	7.58	7.33	7.32
3	7.44	7.47	7.00	6.79	6.54	6.54
4	6.97	6.95	6.46	6.25	6.00	6.00
5	6.59	6.57	6.07	5.87	5.62	5.62
6		6.43	5.79	5.59	5.34	5.34
8			5.44	5.25	4.99	4.99
10			5.23	5.04	4.78	4.78
12			5.08	4.89	4.63	4.62
14			4.96	4.77	4.51	4.50
16			4.86	4.67	4.41	4.41
18			4.78	4.60	4.33	4.33
20			4.71	4.53	4.27	4.26
22			4.66	4.48	4.21	4.20
24			4.61	4.43	4.16	4.16
26			4.57	4.39	4.12	4.11
28			4.53	4.35	4.08	4.08
30			4.50	4.32	4.05	4.04
32			4.47	4.29	4.02	4.01
34			4.44	4.26	3.99	3.99
36			4.42	4.24	3.97	3.96
38			4.39	4.21	3.95	3.94
40			4.37	4.19	3.93	3.92
42			4.35	4.18	3.91	3.90
44			4.34	4.16	3.90	3.88
46			4.32	4.14	3.88	3.87
48			4.31	4.13	3.86	3.85
50			4.29	4.11	3.85	3.84
52			4.28	4.10	3.84	3.83
54			4.27	4.09	3.82	3.82
56			4.26	4.08	3.81	3.80
58			4.24	4.07	3.80	3.79
60			4.23	4.06	3.79	3.78
62			4.23	4.05	3.78	3.77
64			4.22	4.04	3.77	3.76
66			4.21	4.03	3.76	3.76
68			4.20	4.02	3.76	3.75
70			4.19	4.01	3.75	3.74
72			4.18	4.01	3.74	3.73
74			4.18	4.00	3.73	3.73
76			4.17	3.99	3.73	3.72
78			4.16	3.99	3.72	3.71
80			4.16	3.98	3.71	3.71

82	4.15	3.98	3.71	3.70
84	4.15	3.97	3.70	3.70
86	4.14	3.96	3.70	3.69
88	4.14	3.96	3.69	3.68
90	4.13	3.95	3.69	3.68
92	4.13	3.95	3.68	3.67
94	4.12	3.95	3.68	3.67
96	4.12	3.94	3.67	3.67
98	4.11	3.94	3.67	3.66
100	4.11	3.93	3.67	3.66

TABLE S8. Vertical electron affinity (in eV) for the lowest singlet state of n-acene as a function of the acene length, calculated by various functionals in spin-unrestricted TAO-DFT. The experimental data are taken from the compilation in Ref. [10], and the CCSD(T)/CBS data are taken from Ref. [12].

			TAO-DFT			
n-acene	Experiment	CCSD(T)/CBS	LDA	PBE	BLYP	BLYP-D
2	-0.20	-0.48	-0.62	-0.72	-0.94	-0.94
3	0.53	0.28	0.28	0.16	-0.07	-0.07
4	1.07	0.82	0.90	0.77	0.52	0.52
5	1.39	1.21	1.34	1.20	0.95	0.95
6		1.47	1.66	1.52	1.26	1.26
8			2.06	1.92	1.66	1.65
10			2.30	2.15	1.90	1.89
12			2.48	2.33	2.07	2.06
14			2.61	2.46	2.20	2.20
16			2.72	2.57	2.31	2.30
18			2.81	2.66	2.40	2.39
20			2.89	2.73	2.47	2.46
22			2.95	2.79	2.53	2.52
24			3.00	2.84	2.58	2.58
26			3.05	2.89	2.63	2.62
28			3.09	2.93	2.67	2.66
30			3.13	2.97	2.71	2.70
32			3.16	3.00	2.74	2.73
34			3.19	3.03	2.77	2.76
36			3.22	3.06	2.79	2.79
38			3.25	3.08	2.82	2.81
40			3.27	3.10	2.85	2.83
42			3.29	3.12	2.87	2.85
44			3.31	3.14	2.88	2.87
46			3.33	3.16	2.90	2.89
48			3.34	3.18	2.91	2.90
50			3.36	3.19	2.93	2.92
52			3.37	3.21	2.94	2.93
54			3.39	3.22	2.95	2.95
56			3.40	3.23	2.97	2.96
58			3.41	3.24	2.98	2.97
60			3.42	3.25	2.99	2.98
62			3.43	3.26	3.00	2.99
64			3.44	3.27	3.01	3.00

66	3.45	3.28	3.02	3.01
68	3.46	3.29	3.03	3.02
70	3.47	3.30	3.04	3.03
72	3.48	3.31	3.04	3.04
74	3.48	3.32	3.05	3.04
76	3.49	3.32	3.06	3.05
78	3.50	3.33	3.07	3.06
80	3.51	3.34	3.07	3.06
82	3.51	3.34	3.08	3.07
84	3.52	3.35	3.08	3.08
86	3.52	3.36	3.09	3.08
88	3.53	3.36	3.10	3.09
90	3.54	3.37	3.10	3.09
92	3.54	3.37	3.11	3.10
94	3.55	3.38	3.11	3.10
96	3.55	3.38	3.12	3.11
98	3.56	3.39	3.12	3.11
100	3.56	3.39	3.13	3.12

TABLE S9. Fundamental gap (in eV) for the lowest singlet state of n-acene as a function of the acene length, calculated by various functionals in spin-unrestricted TAO-DFT. The experimental data are taken from the compilation in Ref. [10], and the CCSD(T)/CBS data are taken from Refs. [11, 12].

			TAO-DFT			
n-acene	Experiment	CCSD(T)/CBS	LDA	PBE	BLYP	BLYP-D
2	8.34	8.72	8.43	8.30	8.27	8.26
3	6.91	7.19	6.73	6.63	6.61	6.61
4	5.90	6.13	5.56	5.49	5.48	5.48
5	5.20	5.37	4.73	4.67	4.67	4.67
6		4.96	4.13	4.08	4.08	4.08
8			3.38	3.33	3.33	3.33
10			2.93	2.89	2.89	2.89
12			2.60	2.56	2.56	2.56
14			2.34	2.31	2.30	2.31
16			2.13	2.11	2.10	2.10
18			1.97	1.94	1.94	1.94
20			1.83	1.80	1.80	1.80
22			1.71	1.68	1.68	1.68
24			1.60	1.58	1.58	1.58
26			1.52	1.49	1.49	1.49
28			1.44	1.42	1.41	1.42
30			1.37	1.35	1.34	1.35
32			1.30	1.29	1.28	1.28
34			1.25	1.23	1.23	1.23
36			1.20	1.18	1.18	1.18
38			1.15	1.13	1.13	1.13
40			1.11	1.09	1.09	1.09
42			1.07	1.05	1.05	1.05
44			1.03	1.02	1.01	1.01
46			1.00	0.98	0.98	0.98
48			0.96	0.95	0.95	0.95

50	0.94	0.92	0.92	0.92
52	0.91	0.90	0.89	0.89
54	0.88	0.87	0.87	0.87
56	0.86	0.85	0.85	0.85
58	0.84	0.82	0.82	0.82
60	0.81	0.80	0.80	0.80
62	0.79	0.78	0.78	0.78
64	0.77	0.76	0.76	0.76
66	0.76	0.75	0.75	0.75
68	0.74	0.73	0.73	0.73
70	0.72	0.71	0.71	0.71
72	0.71	0.70	0.70	0.70
74	0.69	0.68	0.68	0.68
76	0.68	0.67	0.67	0.67
78	0.67	0.66	0.66	0.66
80	0.65	0.64	0.64	0.64
82	0.64	0.63	0.63	0.63
84	0.63	0.62	0.62	0.62
86	0.62	0.61	0.61	0.61
88	0.61	0.60	0.60	0.60
90	0.59	0.59	0.59	0.59
92	0.58	0.58	0.58	0.58
94	0.58	0.57	0.57	0.57
96	0.57	0.56	0.56	0.56
98	0.56	0.55	0.55	0.55
100	0.55	0.54	0.54	0.54

TABLE S10. Symmetrized von Neumann entropy for the lowest singlet state of n-acene as a function of the acene length, calculated by various functionals in spin-restricted TAO-DFT.

	TAO-DFT			
n-acene	LDA	PBE	BLYP	BLYP-D
2	0.00	0.00	0.00	0.00
3	0.03	0.03	0.03	0.03
4	0.15	0.15	0.15	0.15
5	0.40	0.39	0.39	0.39
6	0.75	0.73	0.73	0.72
8	1.34	1.32	1.32	1.31
10	1.67	1.67	1.67	1.66
12	1.98	1.99	2.00	1.99
14	2.36	2.37	2.38	2.37
16	2.75	2.76	2.78	2.77
18	3.13	3.15	3.17	3.15
20	3.50	3.53	3.55	3.54
22	3.88	3.91	3.94	3.92
24	4.26	4.30	4.32	4.31
26	4.63	4.68	4.71	4.69
28	5.01	5.06	5.09	5.08
30	5.39	5.44	5.48	5.46
32	5.77	5.83	5.87	5.85
34	6.14	6.21	6.25	6.23

36	6.52	6.59	6.64	6.62
38	6.90	6.98	7.03	7.00
40	7.27	7.36	7.41	7.39
42	7.65	7.74	7.80	7.77
44	8.03	8.13	8.18	8.16
46	8.41	8.51	8.57	8.54
48	8.78	8.89	8.96	8.93
50	9.16	9.27	9.34	9.31
52	9.54	9.66	9.73	9.70
54	9.92	10.04	10.11	10.08
56	10.29	10.42	10.50	10.47
58	10.67	10.80	10.89	10.85
60	11.05	11.19	11.27	11.23
62	11.42	11.57	11.66	11.62
64	11.80	11.95	12.04	12.00
66	12.18	12.34	12.43	12.39
68	12.56	12.72	12.81	12.77
70	12.93	13.10	13.20	13.16
72	13.31	13.48	13.59	13.55
74	13.69	13.87	13.97	13.93
76	14.06	14.25	14.36	14.31
78	14.44	14.63	14.74	14.70
80	14.82	15.01	15.13	15.08
82	15.20	15.40	15.51	15.47
84	15.57	15.78	15.90	15.85
86	15.95	16.16	16.29	16.24
88	16.33	16.55	16.67	16.62
90	16.70	16.93	17.06	17.01
92	17.08	17.31	17.44	17.39
94	17.46	17.69	17.83	17.78
96	17.84	18.08	18.22	18.16
98	18.21	18.46	18.60	18.54
100	18.59	18.84	18.99	18.93