Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Electronic Supplementary Information for: On the method-dependence of transition state asynchronicity in Diels-Alder reactions

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Contents

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1 Supplementary figures

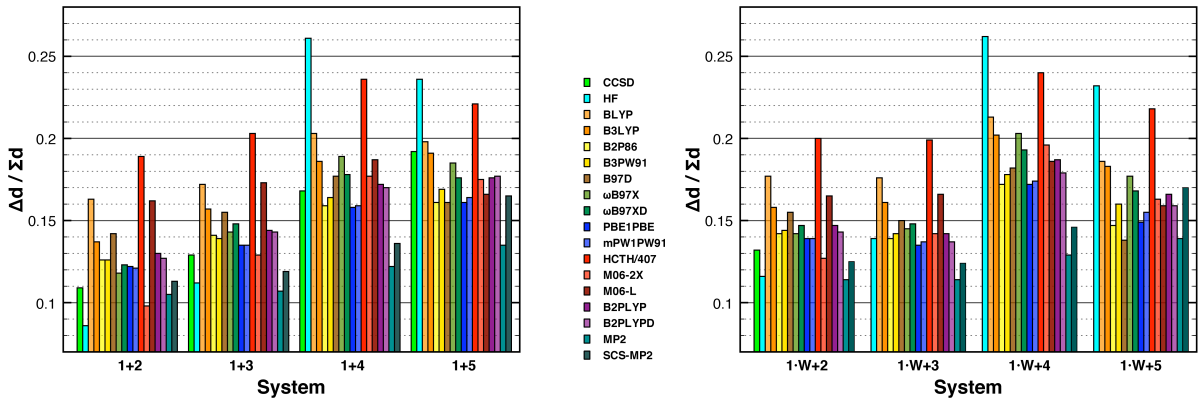

Figure S1: Relative transition state asynchronicity per system, represented by colored bars. $\Delta d/\Sigma d = (d_\alpha - d_\beta)/(d_\alpha + d_\beta)$ No CCSD geometries were optimized for the **1·W+3**, **1·W+4** and **1·W+5** systems.

1 + 2	CCSD	HF	BLYP	B3LYP	B3P86	B3PW91	B97D	ωB97X	ωB97XD	PBE1PBE	mPW1PW91	HCTH/407	M06-2X	M06-L	B2PLYP	B2PLYPD	MP2	10xRMSD [Å]
CCSD	0.00	0.66	0.96	0.58	0.52	0.54	0.58	0.22	0.30	0.49	0.46	1.48	0.36	1.05	0.41	0.42	0.57	CCSD
HF	0.66	0.00	1.20	0.81	0.99	0.90	1.04	0.84	0.85	0.97	0.89	1.59	0.96	1.62	0.92	1.04	1.19	HF
BLYP	0.96	1.20	0.00	0.42	0.59	0.50	0.47	0.89	0.74	0.63	0.60	0.56	1.14	0.89	0.63	0.81	1.07	BLYP
B3LYP	0.58	0.81	0.42	0.00	0.36	0.22	0.33	0.56	0.42	0.38	0.31	0.92	0.82	0.94	0.36	0.57	0.84	B3LYP
B3P86	0.52	0.99	0.59	0.36	0.00	0.17	0.19	0.39	0.24	0.05	0.10	1.11	0.60	0.68	0.15	0.29	0.51	B3P86
B3PW91	0.54	0.90	0.50	0.22	0.17	0.00	0.23	0.46	0.31	0.18	0.12	1.01	0.70	0.81	0.23	0.43	0.66	B3PW91
B97D	0.58	1.04	0.47	0.33	0.19	0.23	0.00	0.46	0.32	0.23	0.24	1.02	0.69	0.65	0.19	0.34	0.61	B97D
ωB97X	0.22	0.84	0.89	0.56	0.39	0.46	0.46	0.00	0.17	0.36	0.36	1.42	0.29	0.84	0.28	0.23	0.42	ωB97X
ωB97XD	0.30	0.85	0.74	0.42	0.24	0.31	0.32	0.17	0.00	0.22	0.21	1.27	0.43	0.79	0.13	0.21	0.46	ωB97XD
PBE1PBE	0.49	0.97	0.63	0.38	0.05	0.18	0.23	0.36	0.22	0.00	0.09	1.16	0.56	0.70	0.15	0.28	0.48	PBE1PBE
mPW1PW91	0.46	0.89	0.60	0.31	0.10	0.12	0.24	0.36	0.21	0.09	0.00	1.13	0.59	0.78	0.15	0.33	0.55	mPW1PW91
HCTH/407	1.48	1.59	0.56	0.92	1.11	1.01	1.02	1.42	1.27	1.16	1.13	0.00	1.68	1.29	1.17	1.35	1.60	HCTH/407
M06-2X	0.36	0.96	1.14	0.82	0.60	0.70	0.69	0.29	0.43	0.56	0.59	1.68	0.00	0.95	0.52	0.38	0.33	M06-2X
M06-L	1.05	1.62	0.89	0.94	0.68	0.81	0.65	0.84	0.79	0.70	0.78	1.29	0.95	0.00	0.71	0.64	0.72	M06-L
B2PLYP	0.41	0.92	0.63	0.36	0.15	0.23	0.19	0.28	0.13	0.15	0.15	1.17	0.52	0.71	0.00	0.22	0.50	B2PLYP
B2PLYPD	0.42	1.04	0.81	0.57	0.29	0.43	0.34	0.23	0.21	0.28	0.33	1.35	0.38	0.64	0.22	0.00	0.31	B2PLYPD
MP2	0.57	1.19	1.07	0.84	0.51	0.66	0.61	0.42	0.46	0.48	0.55	1.60	0.33	0.72	0.50	0.31	0.00	MP2
	CCSD	HF	BLYP	B3LYP	B3P86	B3PW91	B97D	ωB97X	ωB97XD	PBE1PBE	mPW1PW91	HCTH/407	M06-2X	M06-L	B2PLYP	B2PLYPD	MP2	

Figure S2: 2-dimensional all-carbon RMSD matrices for the five systems optimized with CCSD. All figures have been scaled by a factor 10 for clarity.

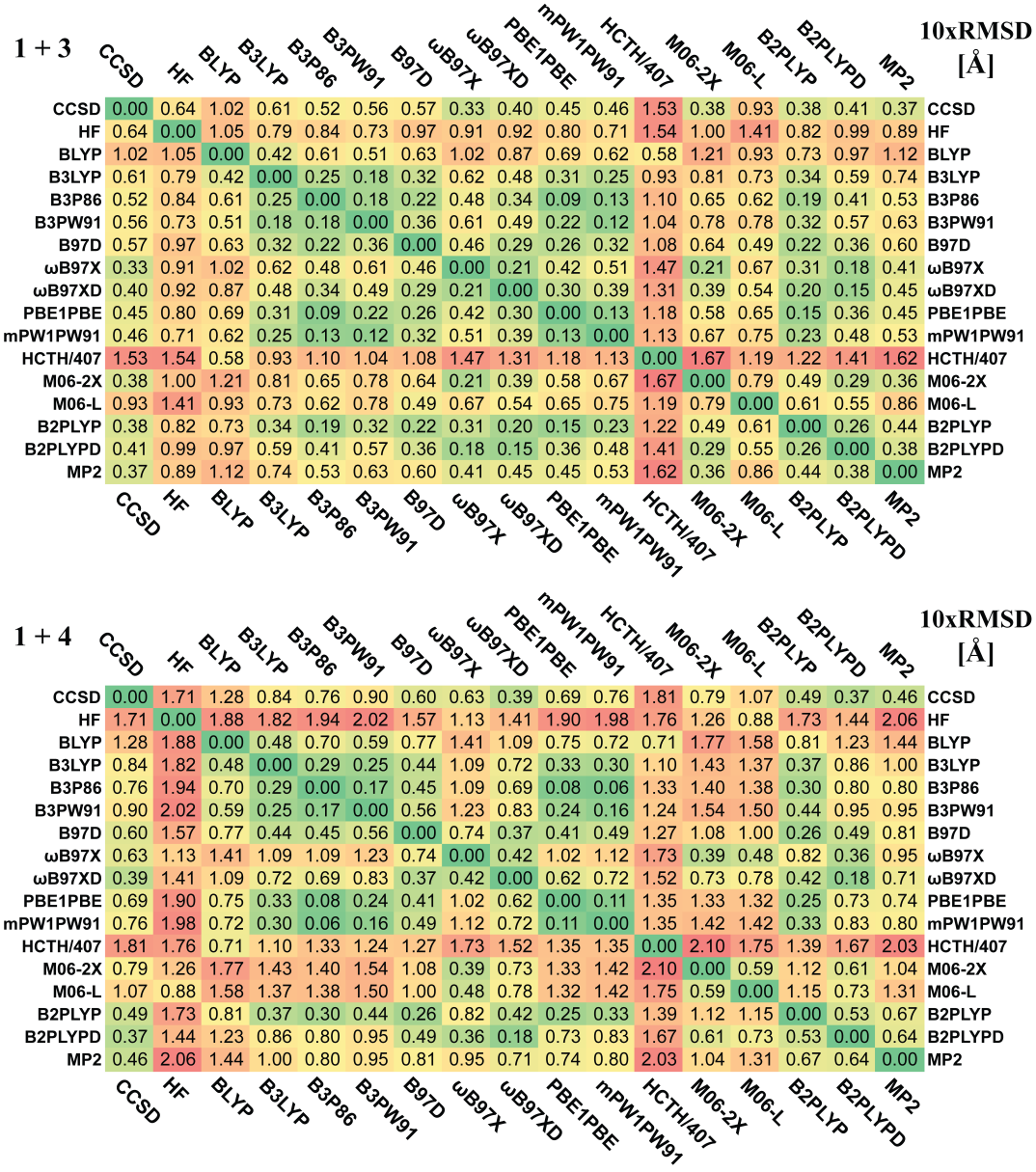

Figure S2 (continued)

1 + 5 — 10xRMSD [Å]

	CCSD	HF	BLYP	B3LYP	B3P86	B3PW91	B97D	ωB97X	ωB97XD	PBE1PBE	mPW1PW91	HCTH/407	M06-2X	M06-L	B2PLYP	B2PLYPD	MP2	
CCSD	0.00	0.71	0.78	0.50	0.59	0.64	0.45	0.20	0.30	0.58	0.59	1.36	0.25	0.39	0.33	0.32	0.62	CCSD
HF	0.71	0.00	0.64	0.57	0.86	0.81	0.87	0.67	0.74	0.85	0.84	0.91	0.84	0.91	0.74	0.92	1.28	HF
BLYP	0.78	0.64	0.00	0.33	0.56	0.46	0.63	0.73	0.71	0.56	0.55	0.72	0.89	0.89	0.56	0.82	1.11	BLYP
B3LYP	0.50	0.57	0.33	0.00	0.37	0.28	0.40	0.45	0.44	0.35	0.32	0.91	0.61	0.67	0.29	0.57	0.85	B3LYP
B3P86	0.59	0.86	0.56	0.37	0.00	0.20	0.35	0.48	0.38	0.04	0.12	1.16	0.57	0.62	0.28	0.46	0.68	B3P86
B3PW91	0.64	0.81	0.46	0.28	0.20	0.00	0.39	0.57	0.50	0.18	0.11	1.01	0.68	0.74	0.34	0.59	0.78	B3PW91
B97D	0.45	0.87	0.63	0.40	0.35	0.39	0.00	0.40	0.35	0.33	0.34	1.23	0.45	0.48	0.24	0.32	0.57	B97D
ωB97X	0.20	0.67	0.73	0.45	0.48	0.57	0.40	0.00	0.15	0.47	0.50	1.32	0.19	0.35	0.27	0.28	0.64	ωB97X
ωB97XD	0.30	0.74	0.71	0.44	0.38	0.50	0.35	0.15	0.00	0.37	0.42	1.32	0.25	0.38	0.22	0.23	0.60	ωB97XD
PBE1PBE	0.58	0.85	0.56	0.35	0.04	0.18	0.33	0.47	0.37	0.00	0.10	1.15	0.56	0.62	0.27	0.45	0.67	PBE1PBE
mPW1PW91	0.59	0.84	0.55	0.32	0.12	0.11	0.34	0.50	0.42	0.10	0.00	1.11	0.60	0.66	0.28	0.50	0.69	mPW1PW91
HCTH/407	1.36	0.91	0.72	0.91	1.16	1.01	1.23	1.32	1.32	1.15	1.11	0.00	1.49	1.49	1.19	1.45	1.71	HCTH/407
M06-2X	0.25	0.84	0.89	0.61	0.57	0.68	0.45	0.19	0.25	0.56	0.60	1.49	0.00	0.29	0.38	0.23	0.55	M06-2X
M06-L	0.39	0.91	0.89	0.67	0.62	0.74	0.48	0.35	0.38	0.62	0.66	1.49	0.29	0.00	0.45	0.28	0.58	M06-L
B2PLYP	0.33	0.74	0.56	0.29	0.28	0.34	0.24	0.27	0.22	0.27	0.28	1.19	0.38	0.45	0.00	0.28	0.59	B2PLYP
B2PLYPD	0.32	0.92	0.82	0.57	0.46	0.59	0.32	0.28	0.23	0.45	0.50	1.45	0.23	0.28	0.28	0.00	0.41	B2PLYPD
MP2	0.62	1.28	1.11	0.85	0.68	0.78	0.57	0.64	0.60	0.67	0.69	1.71	0.55	0.58	0.59	0.41	0.00	MP2

1·W + 2 — 10xRMSD [Å]

	CCSD	HF	BLYP	B3LYP	B3P86	B3PW91	B97D	ωB97X	ωB97XD	PBE1PBE	mPW1PW91	HCTH/407	M06-2X	M06-L	B2PLYP	B2PLYPD	MP2	
CCSD	0.00	0.67	1.05	0.67	0.54	0.60	0.54	0.23	0.35	0.51	0.49	1.56	0.46	0.94	0.40	0.40	0.60	CCSD
HF	0.67	0.00	1.12	0.79	0.94	0.85	0.97	0.84	0.88	0.92	0.86	1.55	1.09	1.53	0.85	1.02	1.22	HF
BLYP	1.05	1.12	0.00	0.40	0.67	0.53	0.64	0.97	0.82	0.70	0.67	0.53	1.32	1.16	0.73	0.99	1.33	BLYP
B3LYP	0.67	0.79	0.40	0.00	0.40	0.23	0.40	0.63	0.49	0.42	0.36	0.90	1.00	1.03	0.41	0.69	1.04	B3LYP
B3P86	0.54	0.94	0.67	0.40	0.00	0.19	0.19	0.41	0.24	0.04	0.08	1.16	0.73	0.74	0.17	0.38	0.69	B3P86
B3PW91	0.60	0.85	0.53	0.23	0.19	0.00	0.28	0.53	0.37	0.21	0.15	1.03	0.87	0.90	0.27	0.55	0.86	B3PW91
B97D	0.54	0.97	0.64	0.40	0.19	0.28	0.00	0.40	0.24	0.21	0.22	1.14	0.71	0.67	0.17	0.35	0.70	B97D
ωB97X	0.23	0.84	0.97	0.63	0.41	0.53	0.40	0.00	0.19	0.39	0.40	1.47	0.38	0.72	0.27	0.20	0.50	ωB97X
ωB97XD	0.35	0.88	0.82	0.49	0.24	0.37	0.24	0.19	0.00	0.23	0.24	1.31	0.54	0.69	0.11	0.22	0.58	ωB97XD
PBE1PBE	0.51	0.92	0.70	0.42	0.04	0.21	0.21	0.39	0.23	0.00	0.08	1.19	0.70	0.74	0.17	0.36	0.66	PBE1PBE
mPW1PW91	0.49	0.86	0.67	0.36	0.08	0.15	0.22	0.40	0.24	0.08	0.00	1.16	0.73	0.80	0.16	0.40	0.71	mPW1PW91
HCTH/407	1.56	1.55	0.53	0.90	1.16	1.03	1.14	1.47	1.31	1.19	1.16	0.00	1.81	1.53	1.23	1.47	1.81	HCTH/407
M06-2X	0.46	1.09	1.32	1.00	0.73	0.87	0.71	0.38	0.54	0.70	0.73	1.81	0.00	0.71	0.62	0.37	0.30	M06-2X
M06-L	0.94	1.53	1.16	1.03	0.74	0.90	0.67	0.72	0.69	0.74	0.80	1.53	0.71	0.00	0.73	0.56	0.67	M06-L
B2PLYP	0.40	0.85	0.73	0.41	0.17	0.27	0.17	0.27	0.11	0.17	0.16	1.23	0.62	0.73	0.00	0.29	0.64	B2PLYP
B2PLYPD	0.40	1.02	0.99	0.69	0.38	0.55	0.35	0.20	0.22	0.36	0.40	1.47	0.37	0.56	0.29	0.00	0.39	B2PLYPD
MP2	0.60	1.22	1.33	1.04	0.69	0.86	0.70	0.50	0.58	0.66	0.71	1.81	0.30	0.67	0.64	0.39	0.00	MP2

Figure S2 (continued)