Supporting Information

Importance of Orbital Invariance in Quantifying Electron–Hole Separation and Exciton Size

John M. Herbert* and Aniket Mandal

Department of Chemistry & Biochemistry
The Ohio State University, Columbus, Ohio 43210 USA

September 19, 2024

Contents

List of Figures

*herbert@chemistry.ohio-state.edu

List of Tables

References

[1] Peach, M. J. G.; Benfield, P.; Helgaker, T.; Tozer, D. J. Excitation energies in density functional theory: An evaluation and a diagnostic test. *J. Chem. Phys.* **2008,** *128,* 044118.

[2] Gill, P. M. W.; Johnson, B. G.; Pople, J. A. A standard grid for density-functional calculations. *Chem. Phys. Lett.* **1993,** *209,* 506–512.

[3] Taka, A. A.; Herbert, J. M.; McCaslin, L. M. Ground-state orbital analysis predicts S_1 charge transfer in donor–acceptor materials. *J. Phys. Chem. Lett.* **2023,** *14,* 11063–11068.

[4] Woon, D. E.; Dunning Jr., T. H. Gaussian basis sets for use in correlated molecular calculations. IV. Calculation of static electrical response properties. *J. Chem. Phys.* **1994,** *100,* 2975–2988.

S1 Catastrophic Example: Dipeptide with Diffuse Basis Sets

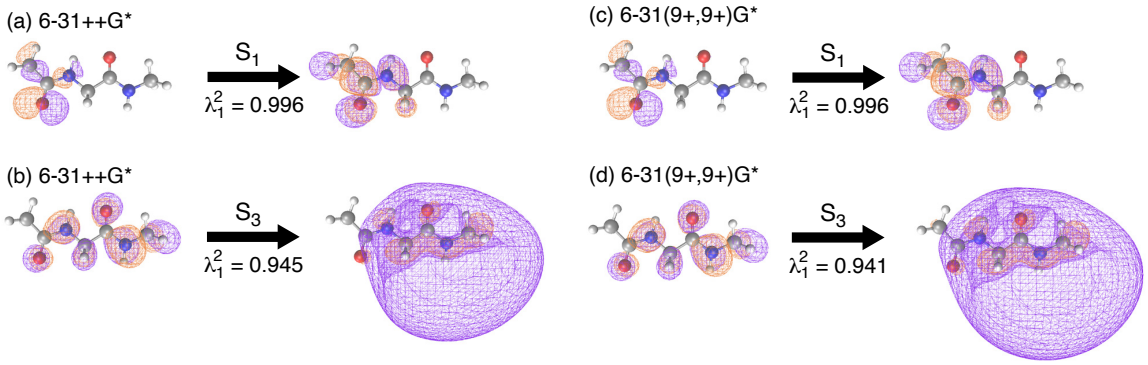

Fig. S1: Principle NTO pairs for (a) $S_0 \rightarrow S_1$ excitation and (b) $S_0 \rightarrow S_3$ excitation of a dipeptide, computed at the CAM-B3LYP/6-31++G* level, in comparison to the (c) $S_0 \rightarrow S_1$ excitation and (d) $S_0 \rightarrow S_3$ computed at the CAM-B3LYP/6-31(9+,9+)G* level. Isocontours encapsulate 90% of $|\psi|^2$ in each case, and results in the two basis sets are nearly indistinguishable.

Table S1: CT metrics (in Å) for two transitions of a dipeptide computed at the TD-CAM-B3LYP/ 6-31(n+,n+)G* level. These are the same transitions considered in Table 1.

n	$S_0 \rightarrow S_1$							$S_0 \rightarrow S_3$						
	ΔE	CMO			NTO			ΔE	CMO			NTO		
	(eV)	Δr	$\Delta\sigma$	Γ	Δr	$\Delta\sigma$	Γ	(eV)	Δr	$\Delta\sigma$	Γ	Δr	$\Delta\sigma$	Γ
0	5.796	1.20	0.40	1.60	3.73	0.52	4.26	7.189	2.17	0.11	2.28	5.06	0.33	5.39
1	5.828	1.46	2.18	3.65	4.50	1.08	5.58	6.258	3.49	1.65	5.14	5.86	1.86	7.73
2	5.813	1.78	4.22	6.01	3.57	1.57	5.14	6.236	4.04	3.80	7.84	9.18	4.29	13.47
3	5.812	2.29	6.25	8.54	6.90	3.65	10.55	6.236	4.48	6.24	10.72	13.58	9.11	22.69
4	5.812	2.30	7.17	9.47	6.14	3.51	9.65	6.236	4.88	8.22	13.11	17.18	14.10	31.28
5	5.812	2.32	7.27	9.59	5.29	2.80	8.09	6.236	4.53	10.24	14.78	21.71	20.35	42.06
6	5.812	2.60	8.10	10.70	5.90	3.26	9.17	6.236	5.20	12.09	17.29	26.99	26.84	53.63
7	5.812	2.25	8.67	10.92	5.89	3.77	9.66	6.236	5.17	13.97	19.14	34.51	43.12	77.64
8	5.812	2.35	9.00	11.35	7.25	6.16	13.41	6.236	5.01	15.49	20.50	36.02	53.08	89.10
9	5.812	2.32	11.17	13.49	6.81	5.64	12.45	6.236	5.22	19.64	24.87	228.29	287.90	516.19

Table S2: CT metrics for two transitions of a dipeptide, computed at the TD-CAM-B3LYP/6-31(n+,n+)G* level. Values of Γ in the CMO and Boys representations are the same as in Table S1.

n	$S_0 \rightarrow S_1$							$S_0 \rightarrow S_3$						
	ΔE	Λ			Γ (Å)			ΔE	Λ			Γ (Å)		
	(eV)	CMO	Boys	NTO	CMO	Boys	NTO	(eV)	CMO	Boys	NTO	CMO	Boys	NTO
0	5.796	0.362	0.055	0.383	1.60	4.26	0.93	7.189	0.415	0.016	0.447	2.28	5.39	1.97
1	5.828	0.312	0.061	0.384	3.65	5.58	1.03	6.258	0.205	0.032	0.326	5.14	7.73	2.51
2	5.813	0.260	0.233	0.384	6.01	5.14	1.05	6.236	0.143	0.017	0.317	7.84	13.47	2.69
3	5.812	0.209	0.025	0.384	8.54	10.55	1.05	6.236	0.121	0.013	0.317	10.72	22.69	2.69
4	5.182	0.194	0.030	0.384	9.47	9.65	1.05	6.236	0.116	0.008	0.317	13.11	31.28	2.69
5	5.182	0.199	0.065	0.384	9.59	8.09	1.05	6.236	0.114	0.010	0.317	14.78	42.06	2.69
6	5.182	0.186	0.086	0.384	10.70	9.17	1.05	6.236	0.114	0.007	0.317	17.29	53.63	2.69
7	5.182	0.198	0.029	0.384	10.92	9.66	1.05	6.236	0.113	0.009	0.317	19.14	77.64	2.70
8	5.182	0.200	0.028	0.384	11.35	13.41	1.06	6.236	0.113	0.006	0.317	20.50	89.10	2.69
9	5.182	0.200	0.031	0.384	13.49	12.45	1.06	6.236	0.113	0.006	0.317	24.87	516.19	2.70

Table S3: CT metrics for two transitions of a dipeptide, computed at the TD-CAM-B3LYP/6-31(n+)G* level.

n	$S_0 \rightarrow S_1$							$S_0 \rightarrow S_3$						
	ΔE	Λ			Γ (Å)			ΔE	Λ			Γ (Å)		
	(eV)	CMO	Boys	NTO	CMO	Boys	NTO	(eV)	CMO	Boys	NTO	CMO	Boys	NTO
0	5.796	0.362	0.055	0.383	1.60	4.26	0.93	7.189	0.415	0.016	0.447	2.28	5.39	1.97
1	5.842	0.345	0.076	0.385	3.30	5.72	0.98	6.430	0.247	0.041	0.349	4.09	7.68	2.09
2	5.820	0.265	0.048	0.384	5.17	7.33	1.04	6.242	0.151	0.024	0.317	6.93	11.75	2.68
3	5.818	0.308	0.208	0.384	5.12	4.26	1.04	6.241	0.123	0.013	0.317	10.10	18.76	2.70
4	5.818	0.261	0.052	0.384	6.95	8.74	1.04	6.241	0.117	0.025	0.317	12.63	13.80	2.69
5	5.818	0.229	0.086	0.384	8.42	8.37	1.04	6.241	0.116	0.007	0.317	14.87	48.90	2.70
6	5.818	0.235	0.044	0.384	8.72	9.23	1.04	6.241	0.115	0.007	0.317	16.57	89.90	2.70
7	5.818	0.233	0.041	0.384	8.57	11.28	1.04	6.241	0.114	0.007	0.317	17.39	88.97	2.70
8	5.818	0.231	0.083	0.384	9.41	10.64	1.04	6.241	0.114	0.007	0.317	19.00	154.45	2.70
9	5.818	0.235	0.108	0.384	10.96	11.16	1.04	6.241	0.114	0.007	0.317	21.58	413.20	2.70

Table S4: Exciton parameters (in Å) for two transition of a dipeptide, computed at the TD-CAM-B3LYP/ 6-31(n+)G* level.

n	$S_0 \rightarrow S_1$					$S_0 \rightarrow S_3$				
	$d_{\text{e-h}}$	d_{exc}	σ_{hole}	σ_{elec}	d_{CD1}	$d_{\text{e-h}}$	d_{exc}	σ_{hole}	σ_{elec}	d_{CD1}
0	0.69	2.03	1.27	1.49	0.91	1.80	3.18	1.98	1.84	1.94
1	0.71	2.09	1.29	1.54	0.96	1.48	3.56	2.23	2.85	2.10
2	0.70	2.14	1.29	1.61	1.02	1.70	4.03	2.32	3.33	2.71
3	0.70	2.15	1.29	1.62	1.02	1.70	4.03	2.31	3.33	2.72
4	0.70	2.15	1.29	1.62	1.02	1.70	4.03	2.31	3.33	2.72
5	0.70	2.15	1.29	1.62	1.03	1.70	4.03	2.31	3.33	2.72
6	0.70	2.15	1.29	1.62	1.03	1.70	4.03	2.31	3.33	2.72
7	0.70	2.15	1.29	1.62	1.03	1.70	4.04	2.31	3.33	2.72
8	0.70	2.15	1.29	1.62	1.03	1.70	4.04	2.31	3.34	2.72
9	0.70	2.15	1.29	1.62	1.03	1.70	4.05	2.31	3.34	2.73

S2 CT Diagnostics: Λ and Γ in Different Representations

S2.1 Numerical Data for the Tozer Set

Table S5: Vertical excitation energies for the Tozer data set.[a]

Molecule	Excitation	Type	TD-DFT/triple-ζ (eV)[b]			Reference
			PBE	PBE0	B3LYP	Value (eV)[c]
Dipeptide	$n_1 \rightarrow \pi_2^*$	CT	4.61	6.65	6.31	8.07
Dipeptide	$\pi_1 \rightarrow \pi_2^*$	CT	5.16	6.40	6.15	7.18
Dipeptide	$n_1 \rightarrow \pi_1^*$	L	5.35	5.62	5.55	5.62
Dipeptide	$n_2 \rightarrow \pi_2^*$	L	5.67	5.86	5.77	5.79
β-dipeptide	$n_1 \rightarrow \pi_2^*$	CT	4.78	7.66	7.26	9.13
β-dipeptide	$\pi_1 \rightarrow \pi_2^*$	CT	5.32	7.82	7.20	7.99
β-dipeptide	$n_1 \rightarrow \pi_1^*$	L	5.38	5.73	5.66	5.40
β-dipeptide	$n_2 \rightarrow \pi_2^*$	L	5.42	5.63	5.56	5.10
Tripeptide	$\pi_1 \rightarrow \pi_2^*$	CT	5.18	6.54	6.27	7.01
Tripeptide	$\pi_2 \rightarrow \pi_3^*$	CT	5.51	6.92	6.60	7.39
Tripeptide	$\pi_1 \rightarrow \pi_3^*$	CT	4.76	6.33	6.06	8.74
Tripeptide	$n_1 \rightarrow \pi_3^*$	CT	4.26	6.51	6.12	9.30
Tripeptide	$n_2 \rightarrow \pi_3^*$	CT	5.16	7.20	6.83	8.33
Tripeptide	$n_1 \rightarrow \pi_2^*$	CT	4.61	6.71	6.33	8.12
Tripeptide	$n_1 \rightarrow \pi_1^*$	L	5.36	5.66	5.57	5.74
Tripeptide	$n_2 \rightarrow \pi_2^*$	L	5.58	5.85	5.74	5.61
Tripeptide	$n_3 \rightarrow \pi_3^*$	L	5.74	5.96	5.88	5.91
Naphthalene	$^1B_{2u}$	L	4.11	4.47	4.38	4.88
Naphthalene	$^1B_{3u}$	L	4.27	4.55	4.47	4.46
Anthracene	$^1B_{2u}$	L	2.94	3.29	3.21	3.69
Anthracene	$^1B_{3u}$	L	3.64	3.94	3.86	3.89
Tetracene	$^1B_{2u}$	L	2.17	2.50	2.43	2.90
Tetracene	$^1B_{3u}$	L	3.24	3.54	3.47	3.52
Pentacene	$^1B_{2u}$	L	1.63	1.95	1.89	2.35
Pentacene	$^1B_{3u}$	L	2.96	3.27	3.21	3.27
Hexacene	$^1B_{2u}$	L	1.23	1.54	1.48	1.95
Hexacene	$^1B_{3u}$	L	2.76	3.08	3.01	3.09
N-phenylpyrrole	$1\,^1B_2$	L	4.33	4.89	4.76	4.85
N-phenylpyrrole	$2\,^1A_1$	L	4.61	5.11	4.96	5.13
N-phenylpyrrole	$2\,^1B_2$	CT	3.98	4.74	4.58	5.47
N-phenylpyrrole	$3\,^1A_1$	CT	3.90	4.82	4.64	5.94
DMABN	^1B	L	4.02	4.54	4.44	4.25
DMABN	^1A	CT	4.30	4.73	4.64	4.56
$H(C_2H_2)_2H$	$1\,^1B_u$	L	5.74	5.96	5.88	5.92
$H(C_2H_2)_3H$	$1\,^1B_u$	L	4.63	4.88	4.81	4.95
$H(C_2H_2)_4H$	$1\,^1B_u$	L	3.93	4.20	4.13	4.41
$H(C_2H_2)_5H$	$1\,^1B_u$	L	3.44	3.73	3.66	4.27

[a]Table is formatted for comparison to Table I of Ref. 1, although the data are from the calculations reported in this work. Continued in Table S6. [b]Computed using $\tau_{\text{ints}} = 10^{-12}$ E_h, $\tau_{\text{shlpr}} = 10^{-12}$ a.u., $\tau_{\text{SCF}} = 10^{-10}$ E_h, $\tau_{\text{CIS}} = 10^{-6}$ E_h, and the SG-1 quadrature grid.[2] For these molecules, the basis set is cc-pVTZ. [c]Benchmark excitation energy from Ref. 1.

Table S6: Vertical excitation energies for the Tozer data set, continued.[a]

Molecule	Excitation	Type	TD-DFT/triple-ζ (eV)[b]			Reference
			PBE	PBE0	B3LYP	Value (eV)[c]
N_2	$^1\Pi_u$	R	11.67	12.37	12.05	13.24
N_2	$^1\Sigma_u^+$	R	10.66	11.94	11.69	12.98
N_2	$^1\Pi_u$	R	10.76	11.97	11.71	12.90
N_2	$^1\Sigma_g^+$	R	10.41	11.55	11.29	12.20
N_2	$^1\Delta_u$	L	10.08	9.88	9.72	10.27
N_2	$^1\Sigma_u^-$	L	9.68	9.36	9.33	9.92
N_2	$^1\Pi_g^-$	L	9.10	9.31	9.26	9.31
CO	$F\,^1\Sigma^+$	R	10.16	11.27	11.03	12.40
CO	$E\,^1\Pi$	R	9.45	10.50	10.28	11.53
CO	$C\,^1\Sigma^+$	R	9.40	10.44	10.20	11.40
CO	$B\,^1\Sigma^+$	R	9.09	10.08	9.86	10.78
CO	$D\,^1\Delta$	L	10.18	10.19	10.03	10.23
CO	$I\,^1\Sigma^-$	L	9.86	9.79	9.72	9.88
CO	$A\,^1\Pi$	L	8.24	8.43	8.39	8.51
H_2CO	$^1A_2$	R	7.43	8.46	8.19	9.22
H_2CO	$^1A_2$	R	6.61	7.64	7.41	8.38
H_2CO	$^1B_1$	L	8.68	8.43	8.83	8.68
H_2CO	$^1B_2$	R	6.50	7.45	7.21	8.12
H_2CO	$^1A_1$	R	6.39	7.40	7.20	7.97
H_2CO	$^1B_2$	R	5.78	6.72	6.47	7.09
H_2CO	$^1A_2$	L	3.73	3.86	3.85	3.94
HCl	$^1\Pi$	CT	7.55	7.90	7.66	8.23

[a]Continued from Table S5. [b]Thresholds are the same as in Table S5 but the basis set is d-aug-cc-pVTZ.[4] [c]Benchmark excitation energy from Ref. 1.

Table S7: Non-invariant metrics for the Tozer data set, computed at the TD-B3LYP/triple-ζ level.[a]

Molecule	Excitation	Type	Error	CMO Representation			Boys Representation			NTO Representation		
			(eV)[b]	Λ	Δr/Å	$\Delta\sigma$/Å	Λ	Δr/Å	$\Delta\sigma$/Å	Λ	Δr/Å	$\Delta\sigma$/Å
Dipeptide	$n_1 \rightarrow \pi_2^*$	CT	−1.76	0.291	2.56	0.23	0.087	5.52	0.87	0.221	3.48	0.17
Dipeptide	$\pi_1 \rightarrow \pi_2^*$	CT	−1.03	0.431	2.21	0.15	0.020	5.96	0.85	0.295	2.57	0.03
Dipeptide	$n_1 \rightarrow \pi_1^*$	L	−0.07	0.378	1.50	0.32	0.484	1.93	0.23	0.425	0.84	0.40
Dipeptide	$n_2 \rightarrow \pi_2^*$	L	−0.02	0.387	1.45	0.22	0.111	4.06	0.86	0.408	0.80	0.30
β-dipeptide	$n_1 \rightarrow \pi_2^*$	CT	−1.87	0.303	3.29	1.64	0.053	6.24	0.81	0.299	3.36	1.50
β-dipeptide	$\pi_1 \rightarrow \pi_2^*$	CT	−0.79	0.608	1.46	0.62	0.043	3.38	0.36	0.615	1.95	0.56
β-dipeptide	$n_1 \rightarrow \pi_1^*$	L	0.26	0.363	1.36	0.95	0.492	1.22	0.37	0.369	0.87	0.38
β-dipeptide	$n_2 \rightarrow \pi_2^*$	L	0.46	0.355	1.91	0.95	0.032	3.37	0.22	0.419	0.81	0.49
Tripeptide	$\pi_1 \rightarrow \pi_2^*$	CT	−0.74	0.435	2.91	0.30	0.003	8.37	0.11	0.424	3.49	0.04
Tripeptide	$\pi_2 \rightarrow \pi_3^*$	CT	−0.79	0.607	1.91	0.59	0.007	6.07	0.07	0.329	3.96	1.12
Tripeptide	$\pi_1 \rightarrow \pi_3^*$	CT	−2.68	0.287	4.58	0.11	0.002	8.91	0.09	0.337	3.53	0.35
Tripeptide	$n_1 \rightarrow \pi_3^*$	CT	−3.18	0.146	5.50	0.42	0.003	8.80	0.06	0.155	5.58	0.72
Tripeptide	$n_2 \rightarrow \pi_3^*$	CT	−1.50	0.396	1.77	0.16	0.016	5.71	0.05	0.167	4.06	0.12
Tripeptide	$n_1 \rightarrow \pi_2^*$	CT	−1.79	0.231	3.39	0.58	0.010	8.44	0.14	0.154	4.57	1.07
Tripeptide	$n_1 \rightarrow \pi_1^*$	L	−0.17	0.295	1.84	0.52	0.046	5.46	0.71	0.341	0.83	0.46
Tripeptide	$n_2 \rightarrow \pi_2^*$	L	0.13	0.323	2.45	0.28	0.014	6.69	0.19	0.414	0.96	0.36
Tripeptide	$n_3 \rightarrow \pi_3^*$	L	−0.03	0.426	1.25	0.15	0.030	4.58	0.06	0.442	0.82	0.10
Naphthalene	$^1B_{2u}$	L	−0.50	0.863	0.00	0.11	0.137	2.64	0.24	0.868	0.00	0.10
Naphthalene	$^1B_{3u}$	L	0.01	0.623	0.00	0.11	0.176	2.41	0.47	0.621	0.00	0.11
Anthracene	$^1B_{2u}$	L	−0.48	0.826	0.00	0.10	0.013	5.85	0.62	0.829	0.00	0.10
Anthracene	$^1B_{3u}$	L	−0.03	0.608	0.00	0.10	0.026	5.15	0.62	0.609	0.00	0.10
Tetracene	$^1B_{2u}$	L	−0.47	0.892	0.00	0.10	0.013	7.76	0.41	0.899	0.00	0.09
Tetracene	$^1B_{3u}$	L	−0.05	0.631	0.00	0.14	0.057	4.14	0.31	0.630	0.00	0.09
Pentacene	$^1B_{2u}$	L	−0.46	0.848	0.00	0.09	0.018	7.45	0.36	0.852	0.00	0.08
Pentacene	$^1B_{3u}$	L	−0.06	0.701	0.00	0.73	0.028	6.60	0.22	0.687	0.00	0.91
Hexacene	$^1B_{2u}$	L	−0.47	0.897	0.00	0.09	0.040	6.44	0.18	0.902	0.00	0.07
Hexacene	$^1B_{3u}$	L	−0.08	0.654	0.00	0.40	0.017	8.05	0.25	0.649	0.00	0.28
N-phenylpyrrole	$1\,^1B_2$	L	−0.09	0.595	1.91	0.67	0.079	3.70	0.19	0.627	1.55	0.51
N-phenylpyrrole	$2\,^1A_1$	L	−0.17	0.591	1.63	0.15	0.048	4.84	0.19	0.583	1.72	0.09
N-phenylpyrrole	$2\,^1B_2$	CT	−0.89	0.522	2.55	0.93	0.013	7.19	0.12	0.491	2.81	0.70
N-phenylpyrrole	$3\,^1A_1$	CT	−1.30	0.344	3.06	0.27	0.023	6.31	0.13	0.386	2.93	0.31
DMABN	^1B	L	−0.19	0.559	0.79	0.64	0.051	4.54	0.66	0.556	0.80	0.61
DMABN	^1A	CT	0.08	0.722	1.37	0.12	0.110	3.59	0.33	0.704	1.54	0.02
$H(C_2H_2)_2H$	$1\,^1B_u$	L	−0.04	0.862	0.00	0.20	0.053	4.37	0.10	0.878	0.00	0.18
$H(C_2H_2)_3H$	$1\,^1B_u$	L	−0.14	0.874	0.00	0.15	0.050	4.48	0.14	0.888	0.00	0.15
$H(C_2H_2)_4H$	$1\,^1B_u$	L	−0.28	0.885	0.00	0.12	0.054	4.51	0.17	0.898	0.00	0.13
$H(C_2H_2)_5H$	$1\,^1B_u$	L	−0.61	0.897	0.00	0.12	0.013	8.94	0.53	0.907	0.00	0.12

[a]These data correspond to the TD-B3LYP calculations reported in Table S5. [b]Relative to reference values listed in Table S5.

Table S8: Non-invariant metrics for the Tozer data set, computed at the TD-B3LYP/triple-ζ level.[a]

Molecule	Excitation	Type	Error	CMO Representation			Boys Representation			NTO Representation		
			(eV)[b]	Λ	Δr/Å	$\Delta\sigma$/Å	Λ	Δr/Å	$\Delta\sigma$/Å	Λ	Δr/Å	$\Delta\sigma$/Å
N_2	$^1\Pi_u$	R	−1.19	0.173	0.00	3.32	0.060	3.64	3.82	0.213	0.00	2.88
N_2	$^1\Sigma_u^+$	R	−1.29	0.113	0.00	5.04	0.049	5.23	5.00	0.160	0.00	4.26
N_2	$^1\Pi_u$	R	−1.19	0.108	0.00	3.88	0.097	2.92	3.89	0.139	0.00	3.57
N_2	$^1\Sigma_g^+$	R	−0.91	0.235	0.00	3.09	0.062	4.28	3.90	0.247	0.00	2.88
N_2	$^1\Delta_u$	L	−0.55	0.870	0.00	0.44	0.069	3.89	4.50	0.890	0.00	0.28
N_2	$^1\Sigma_u^-$	L	−0.59	0.543	0.00	0.45	0.059	4.00	4.50	0.559	0.00	0.25
N_2	$^1\Pi_g^-$	L	−0.05	0.687	0.00	0.24	0.092	2.97	3.92	0.681	0.00	0.11
CO	$F\,^1\Sigma^+$	R	−1.37	0.105	0.93	5.21	0.052	4.724	4.11	0.107	0.17	5.51
CO	$E\,^1\Pi$	R	−1.25	0.141	0.35	5.29	0.058	4.66	4.12	0.175	0.12	4.58
CO	$C\,^1\Sigma^+$	R	−1.20	0.120	1.39	4.92	0.042	3.73	5.34	0.162	1.08	4.23
CO	$B\,^1\Sigma^+$	R	−0.92	0.224	1.11	3.71	0.088	3.20	2.45	0.234	0.95	3.40
CO	$D\,^1\Delta$	L	−0.20	0.760	0.75	0.66	0.076	3.650	2.71	0.795	0.66	0.41
CO	$I\,^1\Sigma^-$	L	−0.16	0.475	0.75	0.67	0.076	3.52	2.71	0.500	0.65	0.38
CO	$A\,^1\Pi$	L	−0.12	0.696	0.35	0.52	0.111	2.74	2.50	0.696	0.24	0.35
H_2CO	$^1A_2$	R	−1.03	0.124	0.70	4.48	0.054	6.02	3.13	0.154	0.35	4.26
H_2CO	$^1A_2$	R	−0.97	0.078	1.40	5.27	0.050	5.29	3.41	0.093	1.14	4.48
H_2CO	$^1A_2$	L	0.15	0.197	1.80	6.31	0.067	3.62	2.00	0.188	1.91	6.90
H_2CO	$^1B_1$	R	−0.91	0.151	1.60	5.24	0.055	5.65	3.62	0.237	0.12	3.47
H_2CO	$^1B_2$	R	−0.77	0.112	1.93	6.81	0.058	4.74	2.05	0.185	1.40	4.24
H_2CO	$^1A_1$	R	−0.62	0.217	2.53	3.21	0.053	5.33	3.49	0.272	1.91	2.29
H_2CO	$^1A_2$	L	−0.09	0.506	0.53	0.25	0.145	2.17	4.33	0.503	0.49	0.11
HCl	$^1\Pi$	CT	−0.57	0.472	1.01	0.63	0.074	2.10	1.61	0.472	0.99	0.60

[a]These data correspond to the TD-B3LYP calculations reported in Table S6. [b]Relative to reference values listed in Table S6.

Table S9: Invariant metrics for the Tozer data set, computed at the TD-B3LYP/triple-ζ level.[a]

Molecule	Excitation	Type	Error (eV)[b]	Metrics (Å)				
				$d_{\text{e-h}}$	d_{exc}	σ_{hole}	σ_{elec}	d_{CD1}
Dipeptide	$n_1 \rightarrow \pi_2^*$	CT	−1.76	3.40	4.27	1.92	1.76	3.56
Dipeptide	$\pi_1 \rightarrow \pi_2^*$	CT	−1.03	2.57	3.50	1.70	1.67	2.59
Dipeptide	$n_1 \rightarrow \pi_1^*$	L	−0.07	0.81	2.33	1.49	1.83	1.15
Dipeptide	$n_2 \rightarrow \pi_2^*$	L	−0.02	0.73	2.50	2.02	1.79	0.96
β-dipeptide	$n_1 \rightarrow \pi_2^*$	CT	−1.87	4.25	5.40	1.32	1.77	5.39
β-dipeptide	$\pi_1 \rightarrow \pi_2^*$	CT	−0.79	1.79	3.97	2.59	2.39	1.99
β-dipeptide	$n_1 \rightarrow \pi_1^*$	L	0.26	0.87	2.24	1.44	1.77	1.20
β-dipeptide	$n_2 \rightarrow \pi_2^*$	L	0.46	0.80	2.30	1.42	1.86	1.25
Tripeptide	$\pi_1 \rightarrow \pi_2^*$	CT	−0.74	3.48	4.58	2.51	2.47	3.53
Tripeptide	$\pi_2 \rightarrow \pi_3^*$	CT	−0.79	3.94	5.24	2.82	1.87	4.90
Tripeptide	$\pi_1 \rightarrow \pi_3^*$	CT	−2.68	3.52	4.57	2.09	2.38	3.81
Tripeptide	$n_1 \rightarrow \pi_3^*$	CT	−3.18	5.49	6.49	2.15	2.41	5.75
Tripeptide	$n_2 \rightarrow \pi_3^*$	CT	−1.50	3.95	4.81	1.98	1.87	4.06
Tripeptide	$n_1 \rightarrow \pi_2^*$	CT	−1.79	4.49	5.44	2.02	2.56	5.03
Tripeptide	$n_1 \rightarrow \pi_1^*$	L	−0.17	0.78	2.42	1.66	2.02	1.13
Tripeptide	$n_2 \rightarrow \pi_2^*$	L	0.13	0.84	2.90	2.57	2.36	1.05
Tripeptide	$n_3 \rightarrow \pi_3^*$	L	−0.03	0.75	2.38	2.15	1.98	0.91
Naphthalene	$^1B_{2u}$	L	−0.50	0.00	3.50	2.35	2.44	0.10
Naphthalene	$^1B_{3u}$	L	0.01	0.00	3.29	2.33	2.44	0.11
Anthracene	$^1B_{2u}$	L	−0.48	0.00	4.21	2.89	2.98	0.10
Anthracene	$^1B_{3u}$	L	−0.03	0.00	3.95	2.85	2.95	0.10
Tetracene	$^1B_{2u}$	L	−0.47	0.00	4.87	3.38	3.47	0.09
Tetracene	$^1B_{3u}$	L	−0.05	0.00	4.59	3.36	3.45	0.09
Pentacene	$^1B_{2u}$	L	−0.46	0.00	5.51	3.84	3.92	0.08
Pentacene	$^1B_{3u}$	L	−0.06	0.00	5.19	3.94	4.49	0.54
Hexacene	$^1B_{2u}$	L	−0.47	0.00	6.11	4.28	4.35	0.07
Hexacene	$^1B_{3u}$	L	−0.08	0.00	5.76	4.35	4.41	0.06
N-phenylpyrrole	$1\,^1B_2$	L	−0.09	1.55	3.70	2.61	2.12	2.05
N-phenylpyrrole	$2\,^1A_1$	L	−0.17	1.70	4.07	2.49	2.55	1.76
N-phenylpyrrole	$2\,^1B_2$	CT	−0.89	2.80	4.17	1.84	2.49	3.45
N-phenylpyrrole	$3\,^1A_1$	CT	−1.30	2.93	4.39	2.09	2.36	3.20
DMABN	^1B	L	0.19	0.80	3.30	2.53	2.03	1.31
DMABN	^1A	CT	0.08	1.53	3.92	2.57	2.58	1.54
$H(C_2H_2)_2H$	$1\,^1B_u$	L	−0.04	0.00	2.97	1.91	2.09	0.18
$H(C_2H_2)_3H$	$1\,^1B_u$	L	−0.14	0.00	3.88	2.54	2.69	0.15
$H(C_2H_2)_4H$	$1\,^1B_u$	L	−0.28	0.00	4.76	3.16	3.29	0.00
$H(C_2H_2)_5H$	$1\,^1B_u$	L	−0.61	0.00	5.61	3.77	3.89	0.12

[a]These data correspond to the TD-B3LYP calculations reported in Table S5. [b]Relative to reference values listed in Table S5.

Table S10: Invariant metrics for the Tozer data set, computed at the TD-B3LYP/triple-ζ level.[a]

Molecule	Excitation	Type	Error (eV)[b]	Metrics (Å)				
				$d_{\text{e-h}}$	d_{exc}	σ_{hole}	σ_{elec}	d_{CD1}
N_2	$^1\Pi_u$	R	−1.19	0.00	3.96	0.95	3.83	2.88
N_2	$^1\Sigma_u^+$	R	−1.29	0.00	5.50	1.16	5.42	4.26
N_2	$^1\Pi_u$	R	−1.19	0.00	4.84	1.16	4.72	3.57
N_2	$^1\Sigma_g^+$	R	−0.91	0.00	4.20	1.16	4.03	2.88
N_2	$^1\Delta_u$	L	−0.55	0.00	1.55	0.94	1.23	0.28
N_2	$^1\Sigma_u^-$	L	−0.59	0.00	1.51	0.94	1.20	0.25
N_2	$^1\Pi_g^-$	L	−0.05	0.00	1.69	1.14	1.25	0.11
CO	$F\,^1\Sigma^+$	R	−1.37	0.17	6.61	1.02	6.53	5.68
CO	$E\,^1\Pi$	R	−1.25	0.12	5.70	1.02	5.61	4.70
CO	$C\,^1\Sigma^+$	R	−1.20	1.08	5.45	1.02	5.26	5.31
CO	$B\,^1\Sigma^+$	R	−0.92	0.95	4.64	1.02	4.43	4.35
CO	$D\,^1\Delta$	L	−0.20	0.66	1.70	0.89	1.30	1.06
CO	$I\,^1\Sigma^-$	L	−0.16	0.64	1.67	0.89	1.27	1.02
CO	$A\,^1\Pi$	L	−0.12	0.22	1.82	1.09	1.44	0.57
H_2CO	$^1A_2$	R	−1.03	0.31	5.68	1.24	5.54	4.62
H_2CO	$^1A_2$	R	−0.97	1.14	5.97	1.24	5.73	5.62
H_2CO	$^1B_1$	L	0.15	0.15	1.90	1.06	1.39	0.15
H_2CO	$^1B_2$	R	−0.91	0.12	4.86	1.24	4.71	3.59
H_2CO	$^1A_1$	R	−0.77	1.40	5.79	1.24	5.48	5.64
H_2CO	$^1B_2$	R	−0.62	1.91	4.20	1.25	3.54	4.20
H_2CO	$^1A_2$	L	−0.09	0.49	1.87	1.23	1.34	0.60
HCl	$^1\Pi$	CT	−0.57	0.99	2.23	1.08	1.68	1.59

[a]These data correspond to the TD-B3LYP calculations reported in Table S6.
[b]Relative to reference values listed in Table S6.

S2.2 Error Correlation Plots

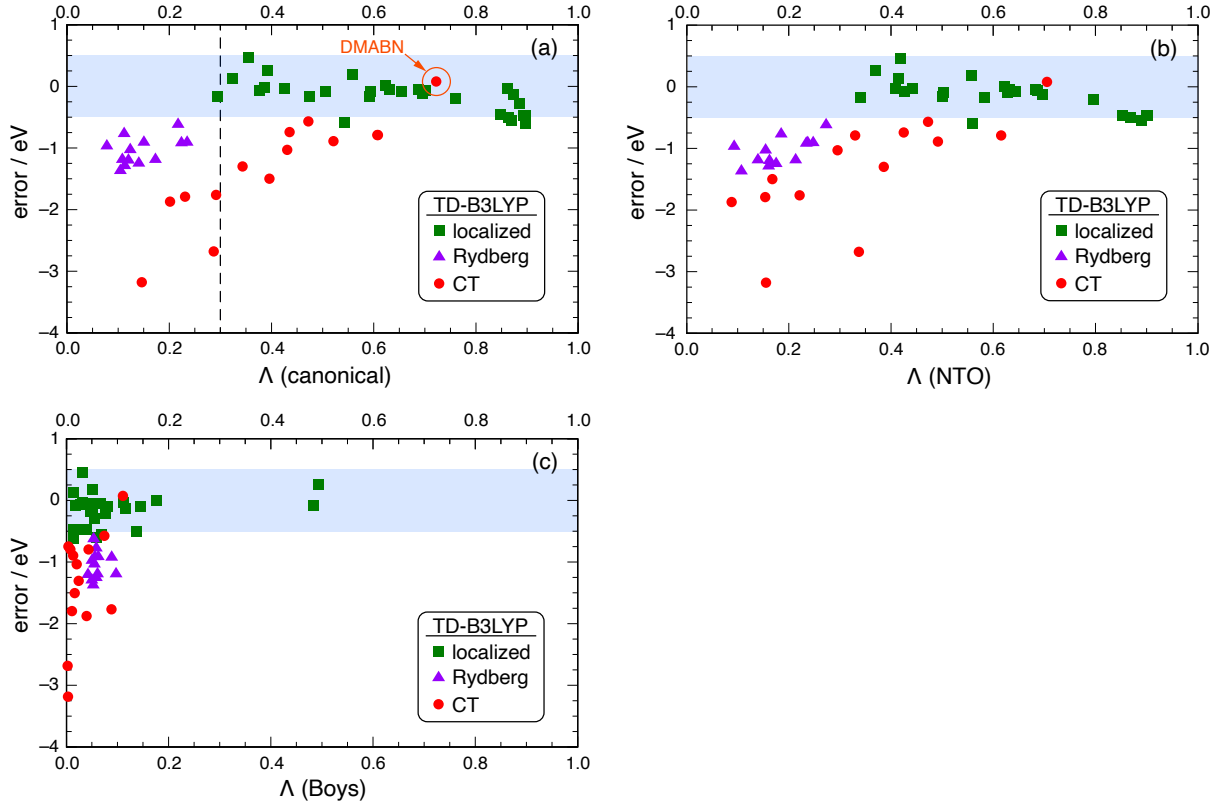

Fig. S2: Errors in vertical excitation energies computed at the TD-B3LYP/triple-ζ level, plotted as a function of the Λ metric in both the (a) CMO, (b) NTO, and (c) Boys-localized representations. The data set is taken from Ref. 1, partitioned into localized, Rydberg, and CT excited states. The basis set is d-aug-cc-pVTZ for N_2, CO, and H_2CO and cc-pVTZ for other molecules. Blue shaded regions delineate where the absolute error is smaller than 0.5 eV. In (a), the data point for the CT transition in the DMABN molecule is indicated explicitly and a suggested threshold value ($\Lambda_{\mathrm{CMO}} = 0.3$) is indicated as well.

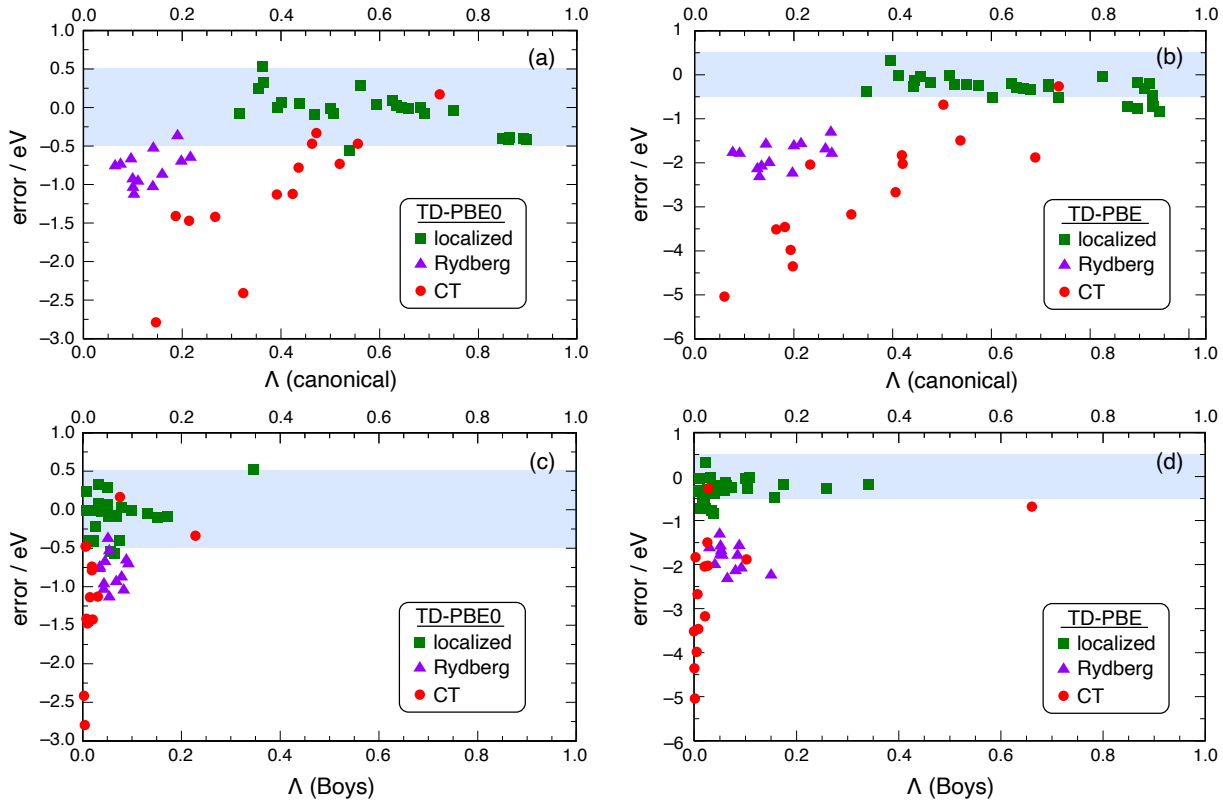

Fig. S3: Errors in vertical excitation energies computed at the TD-PBE/or TD-PBE0/triple-ζ level (as indicated), plotted as a function of the Λ metric in both the CMO and Boys MO representations. The data set is taken from Ref. 1, partitioned into localized, Rydberg, and CT excited states. The basis set is d-aug-cc-pVTZ for N_2, CO, and H_2CO and cc-pVTZ for other molecules. Blue shaded regions delineate where the absolute error is smaller than 0.5 eV; note that the vertical scale is much different for TD-PBE, indicative of much larger errors for CT states. Data in (a) and (c) are the same as those in Fig. 2.

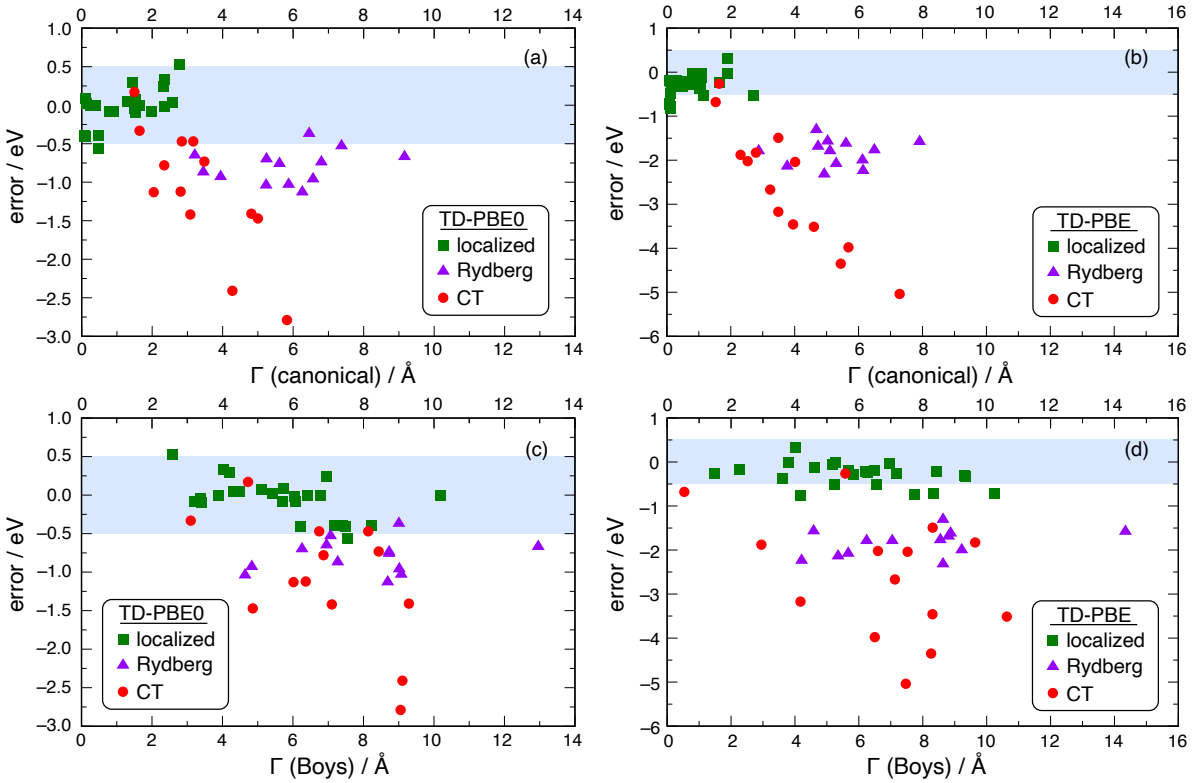

Fig. S4: Errors in vertical excitation energies computed at the TD-PBE/or TD-PBE0/triple-ζ level (as indicated), plotted as a function of the Γ metric in both the CMO and Boys MO representations. The data set is taken from Ref. 1, partitioned into localized, Rydberg, and CT excited states. The basis set is d-aug-cc-pVTZ for N_2, CO, and H_2CO and cc-pVTZ for other molecules. (Note that the scale for Γ is slightly larger for the TD-PBE plots.) Blue shaded regions delineate where the absolute error is smaller than 0.5 eV. Data in (a) and (c) are the same as those in Fig. 4.

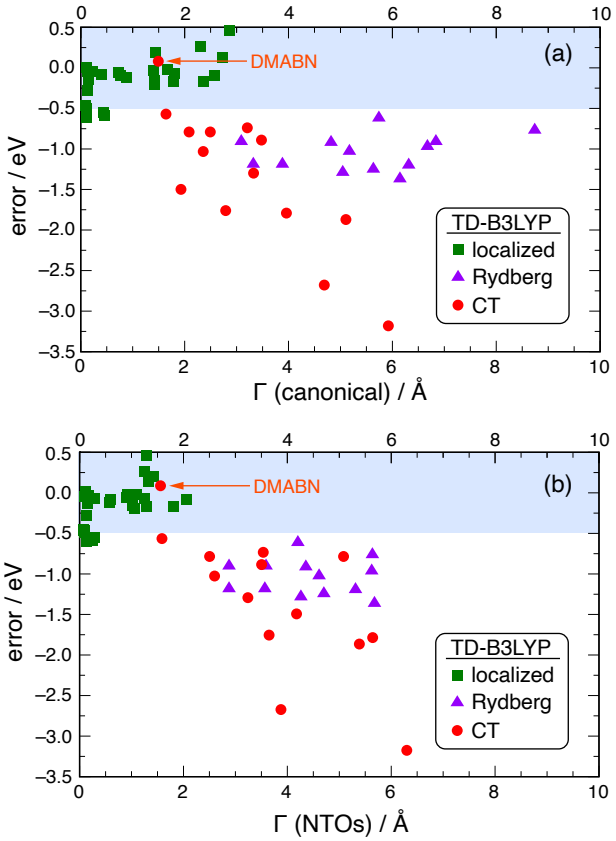

Fig. S5: Errors in vertical excitation energies computed at the TD-B3LYP/triple-ζ level, plotted as a function of (a) Γ_{CMO} or (b) Γ_{NTO}. The data set is from Ref. 1 and the blue shaded region delineates where the absolute error is smaller than 0.5 eV. These are the same data as in Fig. 5.

S3 Cases with Multiple NTO Pairs

S3.1 Linear Acenes

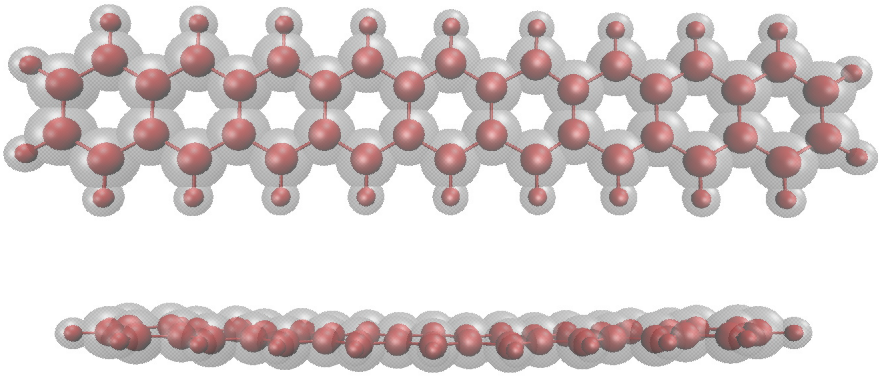

Fig. S6: Overlay of the planar and distorted structures of nonacene from two different viewpoints, with one structure shown in opaque red and the other in translucent gray. One of the structures is planar (D_{2h} symmetry, optimized at the ωB97X-D/6-31G* level) while the other has C_1 symmetry. However, the RMS deviation between the two geometries is only 0.1387 Å when evaluated in the standard nuclear orientation,[2] *i.e.*, the principal axes of nuclear charge coordinate system.

Table S11: Descriptors for excited states of a distorted nonacene molecule with C_1 symmetry, computed at the TD-B3LYP/cc-pVTZ level.

State	ΔE (eV)	Osc. Str.	λ_1^2	Non-Invariant Metrics						Invariant Metrics (Å)			
				CMO			NTO			$d_{\text{e-h}}$	σ_{hole}	σ_{elec}	d_{exc}
				Λ	Δr/Å	Γ/Å	Λ	Δr/Å	Γ/Å				
S_1	0.68	0.012	1.138	0.760	0.55	0.61	0.765	0.60	0.61	0.59	5.74	5.73	7.99
S_2	1.23	0.000	0.834	0.643	0.51	1.74	0.641	0.81	2.34	0.63	6.68	5.72	10.33
S_3	1.36	0.000	0.862	0.626	0.60	1.88	0.625	0.56	1.96	0.31	5.98	6.93	6.71
S_4	2.00	0.039	1.000	0.649	0.52	0.67	0.655	0.30	0.47	0.27	6.99	7.07	8.94
S_5	2.11	0.000	0.689	0.689	1.87	2.87	0.689	1.39	2.28	0.50	6.43	6.10	8.50
S_6	2.35	0.001	0.700	0.665	1.97	2.98	0.668	1.61	2.81	0.82	6.18	6.56	9.79
S_7	2.75	0.000	0.376	0.645	1.09	1.84	0.609	1.67	3.81	0.25	6.92	6.66	7.99
S_8	2.88	0.000	0.459	0.650	0.89	1.67	0.651	0.85	1.86	0.22	7.00	6.29	11.66
S_9	2.90	0.000	0.536	0.602	1.48	1.84	0.599	1.43	1.83	0.49	6.80	7.13	7.27
S_{10}	2.96	0.061	0.601	0.568	3.26	3.66	0.584	1.53	1.72	0.36	5.80	5.83	7.28
S_{11}	3.15	0.000	0.780	0.664	0.89	2.14	0.662	1.12	2.44	1.07	6.05	6.83	9.83
S_{12}	3.37	0.000	0.514	0.653	0.54	1.58	0.652	0.44	1.19	0.26	6.91	6.46	6.22
S_{13}	3.45	0.001	0.379	0.652	2.34	4.03	0.671	1.01	2.26	0.29	7.26	6.93	6.04
S_{14}	3.52	4.426	0.604	0.578	3.46	3.87	0.559	4.45	4.88	0.60	6.27	6.48	9.31
S_{15}	3.59	0.002	0.725	0.678	0.48	0.83	0.654	0.55	1.36	0.09	6.94	6.86	10.79
S_{16}	3.65	0.004	0.556	0.640	0.32	0.90	0.635	0.61	1.37	0.58	6.82	6.81	6.56
S_{17}	3.75	0.003	0.563	0.630	0.33	1.24	0.599	2.06	3.50	0.60	6.27	6.65	9.32
S_{18}	3.80	0.002	0.569	0.646	0.55	1.39	0.646	2.63	3.35	1.67	6.21	6.17	7.78
S_{19}	3.81	0.160	0.497	0.607	2.61	4.13	0.431	9.45	9.96	0.13	7.33	6.41	11.68
S_{20}	3.91	0.062	0.842	0.718	0.24	0.36	0.713	0.41	0.46	0.14	6.81	6.83	11.53
S_{21}	3.97	0.564	0.539	0.696	2.07	3.75	0.602	5.85	8.85	1.38	6.38	7.62	11.32
S_{22}	4.06	0.032	0.377	0.649	1.63	3.02	0.640	2.56	4.01	0.93	7.13	6.77	6.75
S_{23}	4.07	0.002	0.662	0.600	2.35	3.36	0.646	0.79	2.35	0.54	5.96	4.37	6.16
S_{24}	4.14	0.000	0.555	0.640	1.35	2.20	0.627	3.05	3.33	3.03	6.09	6.32	7.55
S_{25}	4.16	0.000	0.748	0.567	0.98	1.59	0.472	3.67	5.10	2.82	5.70	5.08	6.85
S_{26}	4.20	0.000	0.431	0.629	0.84	1.33	0.598	1.79	2.66	1.01	6.99	6.68	10.64
S_{27}	4.24	0.000	0.760	0.559	1.14	1.89	0.517	3.44	4.59	2.85	5.91	5.08	7.81
S_{28}	4.32	0.000	0.564	0.596	1.08	1.46	0.585	0.71	1.40	0.34	6.93	7.00	9.41
S_{29}	4.33	0.370	0.512	0.606	1.62	2.93	0.414	9.95	10.74	0.77	8.02	6.42	12.16
S_{30}	4.51	0.001	0.649	0.673	2.14	2.87	0.674	2.22	2.91	0.27	6.43	6.11	7.90

S3.2 Poly(*p*-Phenylene Vinylene)

Table S12: Descriptors for excited states of a $(PPV)_8$ isomer with two *cis* kinks.[a]

State	ΔE (eV)	λ_1^2	λ_2^2	η_2[b]	Λ		Non-Invariant Measures (Å)				Invariant Measures (Å)				
					CMO	NTO	CMO		NTO		$d_{\text{e-h}}$	d_{CD1}	d_{exc}	σ_{hole}	σ_{elec}
							Δr	Γ	Δr	Γ					
S_1	3.30	0.61	0.26	0.13	0.704	0.744	0.84	1.08	0.07	0.13	0.02	0.05	5.53	7.92	7.96
S_2	3.54	0.47	0.39	0.14	0.655	0.762	2.99	4.60	0.11	0.20	0.03	0.05	5.41	9.69	9.70
S_3	3.88	0.54	0.28	0.18	0.551	0.641	6.55	7.54	0.14	0.29	0.04	0.07	5.12	9.82	9.85
S_4	4.17	0.34	0.25	0.42	0.573	0.623	3.77	5.24	0.26	0.40	0.04	0.06	5.12	10.36	10.37
S_5	4.46	0.27	0.21	0.52	0.574	0.649	3.05	4.29	0.80	1.31	0.17	0.24	4.82	10.37	10.30
S_6	4.56	0.49	0.44	0.07	0.624	0.582	3.92	5.37	3.65	6.45	0.12	0.24	10.14	6.94	7.06
S_7	4.62	0.52	0.23	0.25	0.452	0.471	4.34	5.92	0.54	1.23	0.19	0.42	4.40	5.04	4.81
S_8	4.64	0.46	0.35	0.18	0.423	0.630	6.92	9.02	1.44	1.69	0.32	0.52	5.36	5.78	5.58
S_9	4.66	0.49	0.35	0.16	0.450	0.590	4.78	6.44	0.21	1.08	0.07	0.10	4.25	6.00	6.02
S_{10}	4.67	0.41	0.28	0.32	0.425	0.617	4.81	7.08	0.29	0.83	0.09	0.20	4.30	7.04	7.04

[a]This is an expanded version of the top portion of Table 3, and calculations were performed at the TD-CAM-B3LYP/6-31+G* level. [b]$\eta_2 = 1 - \lambda_1^2 - \lambda_2^2$.

Table S13: Descriptors for excited states of an all-*trans* $(PPV)_6$ isomer.

State	ΔE (eV)	λ_1^2	λ_2^2	η_2[b]	Non-Invariant Metrics (Å)						Invariant Metrics (Å)		
					CMO		Boys		NTO		$d_{\text{e-h}}$	d_{CD1}	d_{exc}
					Δr	Γ	Δr	Γ	Δr	Γ			
S_1	3.18	0.77	0.16	0.07	0.10	0.29	15.86	16.50	0.04	0.11	0.00	0.06	6.12
S_2	3.65	0.48	0.45	0.07	0.62	3.40	16.60	17.77	0.17	0.15	0.00	0.03	5.57
S_3	4.12	0.35	0.33	0.32	0.35	2.48	15.68	16.30	0.14	0.30	0.01	0.05	5.13
S_4	4.48	0.54	0.38	0.08	0.71	3.36	15.98	17.14	0.18	4.16	0.04	0.10	10.46
S_5	4.55	0.54	0.21	0.25	1.59	3.60	16.10	17.00	0.49	0.76	0.04	0.25	4.86
S_6	4.57	0.41	0.26	0.33	0.90	3.03	11.46	12.24	0.80	1.75	0.02	0.28	5.64
S_7	4.66	0.35	0.23	0.42	2.88	5.66	17.51	18.42	0.21	1.21	0.01	0.25	5.37
S_8	4.67	0.31	0.25	0.44	2.94	5.88	16.76	17.52	0.22	0.67	0.01	0.04	4.21
S_9	4.69	0.31	0.24	0.45	2.27	5.56	14.86	15.84	0.26	0.65	0.03	0.17	4.65
S_{10}	4.84	0.45	0.36	0.19	0.46	3.25	13.39	13.85	0.21	4.68	0.03	0.05	9.42

[a]This is an expanded version of the bottom portioin of Table 3, and calculations were performed at the TD-CAM-B3LYP/6-31+G* level. [b]$\eta_2 = 1 - \lambda_1^2 - \lambda_2^2$.

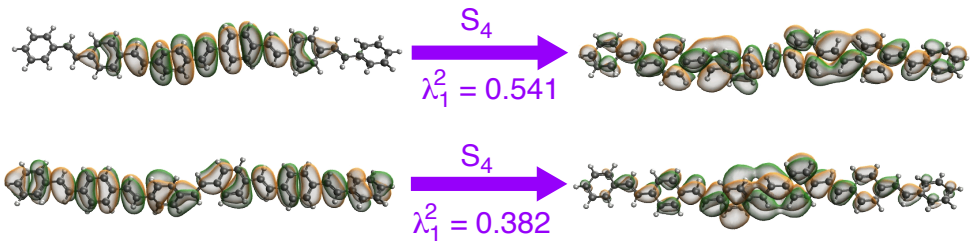

Fig. S7: Principal NTO pairs for the $S_0 \rightarrow S_4$ transition of all-trans $(PPV)_6$, computed at the TD-CAM-B3LYP/6-31+G* and plotted using an isocontour value of 0.02 $a_0^{-3/2}$. Metrics for this state can be found in Table S13.

S3.3 Triazine Benzobisthiadiazole Propeller

Table S14: Descriptors for excited states of a triazine benzobisthiadiazole propeller, computed at the TD-CAM-B3LYP/6-31+G* level. This is a more complete version of Table 4.

State	ΔE (eV)	Osc. Str.	λ_1^2	λ_2^2	Non-Invariant Metrics (Å)				Invariant Metrics (Å)				
					CMO		NTO						
					Δr	Γ	Δr	Γ	$d_{\text{e-h}}$	d_{CD1}	d_{exc}	σ_{hole}	σ_{elec}
S_1	2.595	0.245	0.65	0.18	2.52	3.01	0.15	0.75	0.06	0.52	3.92	4.28	4.74
S_2	2.597	0.244	0.53	0.43	1.75	2.23	0.14	0.63	0.06	0.52	3.91	4.29	4.75
S_3	2.718	0.000	0.33	0.32	1.00	1.51	0.16	0.73	0.00	0.45	3.91	4.78	5.23
S_4	3.435	0.001	0.55	0.45	3.49	3.95	3.69	4.22	0.62	1.09	7.67	4.55	5.02
S_5	3.480	0.001	0.66	0.34	2.94	3.26	4.93	5.83	1.93	2.61	7.89	4.38	5.06
S_6	3.481	0.001	0.68	0.31	1.57	1.89	2.81	3.47	2.11	2.93	7.90	4.25	5.07
S_7	3.568	0.007	0.72	0.25	1.97	2.66	2.84	3.57	1.94	2.75	7.90	4.34	5.15
S_8	3.569	0.007	0.73	0.24	1.99	2.70	3.33	4.18	1.96	2.78	7.89	4.33	5.15
S_9	3.592	0.000	0.66	0.17	0.55	0.99	0.94	1.42	0.52	0.96	8.05	4.71	5.15
S_{10}	3.909	0.193	0.50	0.37	2.51	3.09	0.25	0.64	0.01	0.46	4.00	4.27	4.72

S4 Charge-Transfer Complexes

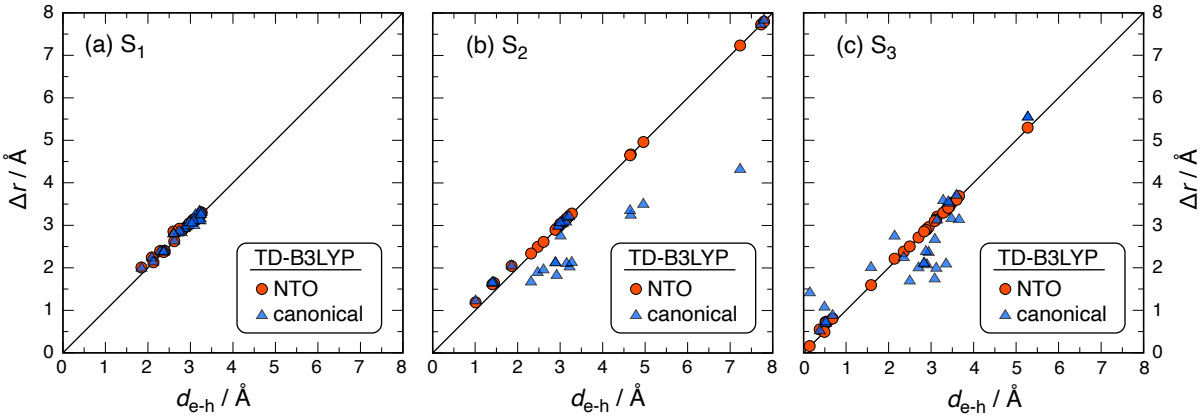

Fig. S8: Correlation between Δr (in either the canonical or the NTO representation) and the invariant metric $d_{\text{e-h}}$, for excitation from S_0 to (a) S_1, (b) S_2, or (c) S_3, for a set of 29 intermolecular CT complexes 3. described at the TD-B3LYP/6-31+G* level. These are the same data as in Fig. 13 but here the scale is the same in each panel.