Electronic Supplementary Material for PCCP

Computation of accurate excitation energies for large organic molecules with double-hybrid density functionals

Electronic Supplementary Information

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1 Complete data for the organic molecule benchmark set

Table S1 contains the complete data for the organic molecule benchmark set for the functionals BP86, B3-LYP, B2-LYP, B2-PLYP, B2GP-LYP and B2GP-PLYP.

Table S1 - Computed[a] vertical singlet excitation energies ΔE (in eV) of all 28 molecules in the organic molecule benchmark set.

Molecule	State	Reference[b]	BP86	B3-LYP	B2-LYP	B2-PLYP	B2GP-LYP	B2GP-PLYP
Ethene	$1^1B_{1u}(\pi \rightarrow \pi^*)$	8.54	−0.81	−0.84	−0.87	−0.70	−0.88	−0.67
E-butadiene	$2^1A_g(\pi \rightarrow \pi^*)$	6.62	−0.32	0.20	1.05	0.57	1.26	1.02
	$1^1B_u(\pi \rightarrow \pi^*)$	6.47	−0.87	−0.73	−0.53	−0.50	−0.47	−0.42
All-*E*-hexatriene	$2^1A_g(\pi \rightarrow \pi^*)$	5.42	−0.35	0.27	1.33	0.55	1.71	0.83
	$1^1B_u(\pi \rightarrow \pi^*)$	5.31	−0.80	−0.62	−0.36	−0.38	−0.29	−0.28
All-*E*-octatetraene	$2^1A_g(\pi \rightarrow \pi^*)$	4.64	−0.45	0.20	1.28	0.50	1.65	0.95
	$1^1B_u(\pi \rightarrow \pi^*)$	4.70	−0.88	−0.68	−0.40	−0.44	−0.31	−0.33
Cyclopropene	$1^1B_2(\pi \rightarrow \pi^*)$	7.06	−0.93	−0.75	−0.56	−0.45	−0.51	−0.35
	$1^1B_1(\sigma \rightarrow \pi^*)$	6.76	−0.46	−0.30	0.03	−0.10	0.16	0.00
Cyclopentadiene	$2^1A_1(\pi \rightarrow \pi^*)$	6.31	−0.22	0.21	0.98	0.34	1.26	0.52
	$3^1A_1(\pi \rightarrow \pi^*)$	8.52	−0.48	−0.37	−0.23	−0.21	−0.19	−0.15
	$1^1B_2(\pi \rightarrow \pi^*)$	5.51	−0.59	−0.49	−0.36	−0.28	−0.33	−0.20
Norbonadiene	$1^1A_2(\pi \rightarrow \pi^*)$	5.34	−0.86	−0.55	−0.17	−0.20	−0.08	−0.06
	$2^1A_2(\pi \rightarrow \pi^*)$	7.45	−0.89	−0.59	−0.01	−0.25	0.18	−0.09
	$1^1B_2(\pi \rightarrow \pi^*)$	6.11	−1.09	−0.59	0.17	−0.19	0.41	0.02
	$2^1B_2(\pi \rightarrow \pi^*)$	7.32	−0.71	−0.45	−0.09	−0.19	0.03	−0.10
Benzene	$1^1B_{1u}(\pi \rightarrow \pi^*)$	6.42	−0.42	−0.32	−0.28	−0.13	−0.30	−0.07
	$1^1B_{2u}(\pi \rightarrow \pi^*)$	5.04	0.20	0.36	0.62	0.19	0.69	0.19
	$1^1E_{1u}(\pi \rightarrow \pi^*)$	7.13	−0.17	−0.06	0.15	−0.02	0.23	0.03
	$1^1E_{2g}(\pi \rightarrow \pi^*)$	8.18	0.10	0.73	1.58	0.91	1.78	1.22
Napthalene	$2^1A_g(\pi \rightarrow \pi^*)$	5.87	−0.02	0.31	0.80	0.24	0.95	0.31
	$3^1A_g(\pi \rightarrow \pi^*)$	6.67	−0.47	0.18	1.09	0.50	1.34	0.77
	$1^1B_{2u}(\pi \rightarrow \pi^*)$	4.77	−0.70	−0.42	−0.10	−0.17	−0.04	−0.04
	$2^1B_{2u}(\pi \rightarrow \pi^*)$	6.33	−0.45	−0.21	0.10	−0.10	0.20	−0.03
	$3^1B_{2u}(\pi \rightarrow \pi^*)$	8.17	−0.64	−0.30	0.33	−0.16	0.58	−0.02
	$1^1B_{3u}(\pi \rightarrow \pi^*)$	4.24	−0.01	0.20	0.49	0.09	0.58	0.11
	$2^1B_{3u}(\pi \rightarrow \pi^*)$	6.06	−0.33	−0.13	0.17	−0.08	0.27	−0.01
	$3^1B_{3u}(\pi \rightarrow \pi^*)$	7.74	0.26	0.91	1.75	1.08	1.94	1.46
	$1^1B_{1g}(\pi \rightarrow \pi^*)$	5.99	−0.95	−0.41	0.32	0.09	0.42	0.24
	$2^1B_{1g}(\pi \rightarrow \pi^*)$	6.47	−0.30	−0.15	0.23	−0.27	0.51	−0.13
Furan	$2^1A_1(\pi \rightarrow \pi^*)$	6.50	−0.12	0.20	0.76	0.17	0.96	0.27
	$3^1A_1(\pi \rightarrow \pi^*)$	8.17	−0.01	0.08	0.26	0.19	0.32	0.25
	$1^1B_2(\pi \rightarrow \pi^*)$	6.39	−0.28	−0.23	−0.17	−0.07	−0.17	−0.01
Pyrrole	$2^1A_1(\pi \rightarrow \pi^*)$	6.31	−0.05	0.22	0.66	0.17	0.80	0.24
	$3^1A_1(\pi \rightarrow \pi^*)$	8.17	−0.32	−0.21	−0.01	−0.12	0.05	−0.06
	$1^1B_2(\pi \rightarrow \pi^*)$	6.33	0.01	0.07	0.15	0.20	0.15	0.25
Imidazole	$2^1A'(\pi \rightarrow \pi^*)$	6.19	0.09	0.26	0.46	0.40	0.50	0.49
	$3^1A'(\pi \rightarrow \pi^*)$	6.93	−0.07	0.11	0.44	0.05	0.55	0.11
	$4^1A'(\pi \rightarrow \pi^*)$	8.16	−0.04	0.11	0.31	−0.10	0.45	0.14
	$1^1A''(n \rightarrow \pi^*)$	6.81	−0.91	−0.35	0.33	−0.08	0.50	0.10
	$2^1A''(n \rightarrow \pi^*)$	7.90	−0.72	−0.45	0.37	−0.31	0.70	−0.21
Pyridine	$2^1A_1(\pi \rightarrow \pi^*)$	6.39	−0.18	−0.08	−0.03	0.11	−0.05	0.17
	$3^1A_1(\pi \rightarrow \pi^*)$	7.46	−0.19	−0.14	0.11	−0.07	0.18	−0.02
	$1^1B_2(\pi \rightarrow \pi^*)$	5.02	0.33	0.47	0.71	0.28	0.77	0.28
	$2^1B_2(\pi \rightarrow \pi^*)$	7.27	−0.14	0.03	0.31	0.04	0.41	0.09
	$1^1B_1(n \rightarrow \pi^*)$	5.17	−0.79	−0.37	0.17	−0.22	0.34	−0.08
	$1^1A_2(n \rightarrow \pi^*)$	5.51	−1.03	−0.40	0.61	−0.30	0.95	−0.10
Pyrazine	$1^1B_{1u}(\pi \rightarrow \pi^*)$	6.89	−0.48	−0.39	−0.36	−0.18	−0.39	−0.12

1 COMPLETE DATA FOR THE ORGANIC MOLECULE BENCHMARK SET

Molecule	State	Reference[b]	BP86	B3-LYP	B2-LYP	B2-PLYP	B2GP-LYP	B2GP-PLYP
	$2^1B_{1u}(\pi \rightarrow \pi^*)$	7.79	−0.26	−0.11	0.11	−0.05	0.17	0.00
	$1^1B_{2u}(\pi \rightarrow \pi^*)$	4.85	0.40	0.52	0.68	0.31	0.73	0.30
	$2^1B_{2u}(\pi \rightarrow \pi^*)$	7.66	0.09	0.12	0.50	0.10	0.63	0.17
	$1^1A_u(n \rightarrow \pi^*)$	4.70	−0.64	−0.01	0.97	0.09	1.31	0.29
	$1^1B_{1g}(n \rightarrow \pi^*)$	6.41	−0.84	−0.03	1.37	0.00	1.88	0.25
	$1^1B_{2g}(n \rightarrow \pi^*)$	5.68	−0.57	−0.13	0.37	0.05	0.50	0.20
	$1^1B_{3u}(n \rightarrow \pi^*)$	4.12	−0.54	−0.16	0.32	−0.01	0.46	0.11
Pyrimidine	$2^1A_1(\pi \rightarrow \pi^*)$	6.63	−0.17	−0.05	0.03	0.13	0.03	0.19
	$3^1A_1(\pi \rightarrow \pi^*)$	7.21	0.11	0.27	0.53	0.29	0.63	0.35
	$1^1B_2(\pi \rightarrow \pi^*)$	5.24	0.35	0.50	0.76	0.28	0.83	0.28
	$2^1B_2(\pi \rightarrow \pi^*)$	7.64	−0.06	0.12	0.34	0.06	0.44	0.11
	$1^1B_1(n \rightarrow \pi^*)$	4.44	−0.64	−0.17	0.48	−0.07	0.70	0.08
	$1^1A_2(n \rightarrow \pi^*)$	4.80	−0.77	−0.20	0.65	−0.08	0.93	0.12
Pyridazine	$2^1A_1(\pi \rightarrow \pi^*)$	5.18	0.28	0.43	0.66	0.19	0.73	0.19
	$3^1A_1(\pi \rightarrow \pi^*)$	7.62	−0.23	−0.12	0.16	−0.07	0.25	−0.02
	$1^1B_2(\pi \rightarrow \pi^*)$	6.31	0.01	0.12	0.15	0.33	0.11	0.40
	$2^1B_2(\pi \rightarrow \pi^*)$	7.29	−0.19	−0.05	0.18	−0.03	0.26	0.03
	$1^1A_2(n \rightarrow \pi^*)$	4.31	−0.77	−0.13	0.79	0.04	1.05	0.30
	$2^1A_2(n \rightarrow \pi^*)$	5.77	−0.76	−0.33	0.33	−0.27	0.59	−0.17
	$1^1B_1(n \rightarrow \pi^*)$	3.78	−0.63	−0.20	0.37	−0.02	0.53	0.14
	$2^1B_1(n \rightarrow \pi^*)$	6.52	−1.07	−0.43	0.55	−0.34	0.90	−0.13
s-triazine	$2^1A_1'(\pi \rightarrow \pi^*)$	7.25	−0.38	−0.24	−0.13	−0.10	−0.13	−0.04
	$1^1A_2'(\pi \rightarrow \pi^*)$	5.79	0.16	0.35	0.69	0.05	0.80	0.05
	$1^1E'(\pi \rightarrow \pi^*)$	7.50	0.13	0.29	0.58	0.30	0.69	0.36
	$1^1A_1''(n \rightarrow \pi^*)$	4.60	−0.76	−0.15	0.79	−0.10	1.10	0.08
	$1^1A_2''(n \rightarrow \pi^*)$	4.66	−0.58	−0.12	0.56	−0.02	0.80	0.13
	$1^1E''(n \rightarrow \pi^*)$	4.70	−0.71	−0.16	0.64	−0.05	0.90	0.12
	$2^1E''(n \rightarrow \pi^*)$	7.71	−1.00	−0.22	0.79	0.08	1.09	0.34
s-tetrazine	$1^1A_u(n \rightarrow \pi^*)$	3.51	−0.64	0.00	0.96	0.11	1.27	0.34
	$2^1A_u(n \rightarrow \pi^*)$	5.50	−0.90	−0.46	0.16	−0.29	0.36	−0.16
	$1^1B_{1g}(n \rightarrow \pi^*)$	4.73	−0.60	0.00	0.65	0.29	0.81	0.49
	$2^1B_{1g}(n \rightarrow \pi^*)$	6.45	−0.58	0.19	1.39	0.08	1.86	0.25
	$3^1B_{1g}(n \rightarrow \pi^*)$	6.73	−0.20	0.67	2.65	0.34	3.38	0.70
	$1^1B_{2g}(n \rightarrow \pi^*)$	5.20	−0.41	0.09	0.64	0.22	0.79	0.38
	$2^1B_{2g}(n \rightarrow \pi^*)$	6.06	−0.82	−0.07	1.33	−0.06	1.84	0.21
	$2^1B_{3g}(\pi \rightarrow \pi^*)$	8.34	0.38	0.96	1.66	0.94	1.83	1.22
	$1^1B_{1u}(\pi \rightarrow \pi^*)$	6.94	−0.12	−0.04	−0.08	0.20	−0.16	0.28
	$2^1B_{1u}(\pi \rightarrow \pi^*)$	7.42	−0.06	0.06	0.30	0.06	0.39	0.12
	$1^1B_{2u}(\pi \rightarrow \pi^*)$	4.93	0.53	0.65	0.82	0.34	0.87	0.32
	$2^1B_{2u}(\pi \rightarrow \pi^*)$	8.14	−0.05	0.12	0.45	0.08	0.57	0.15
	$1^1B_{3u}(n \rightarrow \pi^*)$	2.29	−0.44	−0.05	0.47	0.09	0.62	0.22
	$2^1B_{3u}(n \rightarrow \pi^*)$	6.77	−1.13	−0.48	0.53	−0.31	0.88	−0.09
Formaldehyde	$1^1A_2(n \rightarrow \pi^*)$	3.99	−0.19	−0.10	0.03	−0.14	0.09	−0.10
	$1^1B_1(\sigma \rightarrow \pi^*)$	9.14	−0.34	−0.25	−0.04	−0.18	0.03	−0.11
	$2^1A_1(\pi \rightarrow \pi^*)$	9.32	0.63	−0.15	−0.03	0.07	−0.04	0.13
Acetone	$1^1A_2(n \rightarrow \pi^*)$	4.44	−0.23	−0.10	0.13	−0.13	0.21	−0.08
	$2^1A_1(\pi \rightarrow \pi^*)$	9.31	−0.55	−0.27	−0.31	−0.61	−0.19	−0.38
	$1^1B_1(\sigma \rightarrow \pi^*)$	9.27	−1.12	−0.67	−0.18	−0.42	−0.05	−0.30
p-benzoquinone	$1^1A_u(n \rightarrow \pi^*)$	2.77	−0.74	−0.19	0.48	−0.05	0.67	0.12
	$1^1B_{1g}(n \rightarrow \pi^*)$	2.76	−0.86	−0.33	0.33	−0.15	0.53	0.01
	$1^1B_{1u}(\pi \rightarrow \pi^*)$	5.28	−0.79	−0.45	0.07	−0.21	0.24	−0.07
	$2^1B_{1u}(\pi \rightarrow \pi^*)$	7.92	−1.10	−0.67	−0.16	−0.29	0.00	−0.13
	$1^1B_{3g}(\pi \rightarrow \pi^*)$	4.26	−0.90	−0.53	0.05	−0.08	0.23	0.11
	$2^1B_{3g}(\pi \rightarrow \pi^*)$	6.96	−0.84	−0.37	0.42	−0.13	0.70	0.08
	$1^1B_{3u}(n \rightarrow \pi^*)$	5.64	−1.25	−0.21	1.27	−0.03	1.71	0.44
Formamide	$1^1A''(n \rightarrow \pi^*)$	5.63	−0.17	−0.08	0.17	−0.14	0.27	−0.09
	$2^1A'(\pi \rightarrow \pi^*)$	7.39	0.51	0.74	0.47	−0.24	0.69	0.01
	$3^1A'(\pi \rightarrow \pi^*)$	10.54	0.44	0.38	0.86	0.39	1.04	0.49
Acetamide	$1^1A''(n \rightarrow \pi^*)$	5.69	−0.28	−0.13	0.20	−0.16	0.33	−0.11
	$2^1A'(\pi \rightarrow \pi^*)$	7.27	0.23	0.19	0.92	0.01	0.93	0.12
	$3^1A'(\pi \rightarrow \pi^*)$	10.09	−0.67	−0.08	0.56	−0.10	0.87	0.01
Propanamide	$1^1A''(n \rightarrow \pi^*)$	5.72	−0.29	−0.13	0.20	−0.17	0.33	−0.12
	$2^1A'(\pi \rightarrow \pi^*)$	7.20	0.08	0.56	0.70	−0.29	0.98	0.18

1 COMPLETE DATA FOR THE ORGANIC MOLECULE BENCHMARK SET

Molecule	State	Reference[b]	BP86	B3-LYP	B2-LYP	B2-PLYP	B2GP-LYP	B2GP-PLYP
	$3^1A'(\pi \rightarrow \pi^*)$	9.94	−1.77	−0.94	0.22	−0.39	0.58	−0.11
Cytosine	$2^1A'(\pi \rightarrow \pi^*)$	4.67	−0.47	−0.03	0.56	−0.02	0.74	0.11
	$3^1A'(\pi \rightarrow \pi^*)$	5.53	−0.61	−0.11	0.70	−0.07	0.97	0.09
	$4^1A'(\pi \rightarrow \pi^*)$	6.40	0.09	0.32	0.63	0.11	0.81	0.19
	$5^1A'(\pi \rightarrow \pi^*)$	6.97	−0.60	−0.51	0.55	−0.29	0.90	−0.12
	$1^1A''(n \rightarrow \pi^*)$	5.12	−1.33	−0.36	0.59	−0.15	0.86	0.04
	$2^1A''(n \rightarrow \pi^*)$	5.53	−1.04	−0.42	0.73	0.11	0.93	0.26
Thymine	$2^1A'(\pi \rightarrow \pi^*)$	5.06	−0.46	−0.06	0.45	0.08	0.60	0.22
	$3^1A'(\pi \rightarrow \pi^*)$	6.15	−0.82	−0.18	0.86	0.09	1.13	0.32
	$4^1A'(\pi \rightarrow \pi^*)$	6.53	−0.68	−0.22	0.59	−0.20	0.96	−0.03
	$5^1A'(\pi \rightarrow \pi^*)$	7.43	−0.50	0.04	0.80	−0.08	1.09	0.14
	$1^1A''(n \rightarrow \pi^*)$	4.95	−0.86	−0.25	0.40	−0.19	0.59	−0.05
	$2^1A''(n \rightarrow \pi^*)$	6.38	−1.58	−0.58	0.36	−0.23	0.56	−0.07
	$3^1A''(n \rightarrow \pi^*)$	6.85	−1.52	−0.64	1.01	−0.68	1.63	−0.11
	$4^1A''(n \rightarrow \pi^*)$	7.43	−1.30	−0.74	0.74	−0.77	1.29	−0.49
Uracil	$2^1A'(\pi \rightarrow \pi^*)$	5.23	−0.47	−0.04	0.48	0.07	0.62	0.20
	$3^1A'(\pi \rightarrow \pi^*)$	6.15	−0.94	−0.28	0.84	−0.12	1.19	0.21
	$4^1A'(\pi \rightarrow \pi^*)$	6.74	−0.73	−0.24	0.55	−0.12	0.88	−0.01
	$5^1A'(\pi \rightarrow \pi^*)$	7.42	−0.36	0.03	0.73	−0.03	0.99	0.09
	$1^1A''(n \rightarrow \pi^*)$	4.91	−0.94	−0.28	0.41	−0.20	0.61	−0.04
	$2^1A''(n \rightarrow \pi^*)$	6.28	−1.52	−0.54	0.38	−0.23	0.59	−0.05
	$3^1A''(n \rightarrow \pi^*)$	6.98	−1.74	−0.84	0.90	−0.81	1.51	−0.32
	$4^1A''(n \rightarrow \pi^*)$	7.28	−1.17	−0.64	0.77	−0.82	1.35	−0.50
Adenine	$2^1A'(\pi \rightarrow \pi^*)$	5.20	−0.21	0.07	0.31	−0.02	0.44	0.06
	$3^1A'(\pi \rightarrow \pi^*)$	5.29	−0.72	−0.29	0.41	−0.10	0.55	0.03
	$4^1A'(\pi \rightarrow \pi^*)$	6.34	−0.50	−0.02	0.57	0.12	0.72	0.27
	$5^1A'(\pi \rightarrow \pi^*)$	6.64	−0.37	0.05	0.40	−0.18	0.63	0.02
	$6^1A'(\pi \rightarrow \pi^*)$	6.87	−0.22	0.21	0.48	−0.10	0.68	0.07
	$7^1A'(\pi \rightarrow \pi^*)$	7.56	−0.65	−0.04	0.21	−0.42	0.46	−0.31
	$1^1A''(n \rightarrow \pi^*)$	5.19	−0.89	−0.22	0.69	−0.08	0.98	0.12
	$2^1A''(n \rightarrow \pi^*)$	5.96	−0.91	−0.35	0.44	−0.21	0.69	−0.02

[a] The differences between results and references are shown. The results were obtained with the TZVP basis set. [b] CASPT2/TZVP (see Ref. [20]).

2 Ground state geometries of the organic dye benchmark set

This section contains the electronic ground state geometries of the five molecules in the organic molecule benchmark set. They were obtained at the RI-PBE/TZVP level of theory. The coordinates are given in the standard *TURBOMOLE* format.

RI-PBE/TZVP optimized structure of coumarin 153 (**1**)

```
$coord
    4.01557277164234      4.49129636431285      0.06188954974193      c
    2.59401485445041      2.01549498832286      0.07924781837098      c
    3.88016607200719     -0.33927379015785      0.11390699407797      c
    6.48946535547568     -0.41000086390850      0.09705831863882      n
    7.94484417064227      1.90039410488319      0.49662533491728      c
    6.72856758543468      4.13201680234655     -0.85536496516974      c
   -0.04424107904196      2.01224832697194      0.06165309179965      c
   -1.50212426715539     -0.23585941191907      0.03960710994359      c
   -0.15583644145209     -2.54149781563847      0.06370019271657      c
    2.45322711839317     -2.64128955923113      0.12092327605482      c
   -4.19959314327368      0.04503593332055      0.00265637332315      c
   -5.30511588043156      2.38038193763009     -0.01060660174829      c
   -3.82343070500378      4.67695812147465      0.01883710646257      c
   -1.17196230230311      4.34729270710546      0.05986714935835      o
    7.85017129022474     -2.78692100132785      0.43180169348070      c
    6.46963680392111     -4.97273660546300     -0.83483602549677      c
    3.79429132728674     -5.16302069085760      0.23067518808494      c
   -5.87999699719117     -2.27821770339259     -0.02954106752126      c
   -4.61455320419499      6.82985791414538      0.01326929791170      o
    9.74411418593158     -2.54090967551548     -0.39465817705939      h
    8.12278672711753     -3.20060646206820      2.46964908738083      h
   -1.19520457246355     -4.32105412452064      0.05421823228242      h
   -7.34545290143348      2.62376485696882     -0.04152352797483      h
   -5.49151173250505     -3.75871326132849      2.04741658806261      f
   -8.37366798183493     -1.69207352272784     -0.06953541106832      f
   -5.42268253727562     -3.75132100243704     -2.09756079794448      f
    8.12317334848876      2.31050707114223      2.54484459684157      h
    9.86564115258804      1.56119588598988     -0.22656252504038      h
    2.68561880451126     -6.59181878580590     -0.79558085226734      h
    3.89551372249725     -5.81262983836239      2.21275218949782      h
    6.40482608037497     -4.64534491122287     -2.88986987071482      h
    7.52526909367123     -6.73470627395386     -0.51593590848702      h
    7.85088564742974      5.84789566937283     -0.51461427803544      h
    6.75038534058127      3.77375341866695     -2.90600209330297      h
```

```
    3.00903871310977      5.86486783833983     -1.12724075555016      h
    4.01459618559262      5.30984127109230      1.98182189135085      h
$end
```

RI-PBE/TZVP optimized structure of oxazine 9 (**2**)

```
$coord
    6.48262754805472      5.06710813676903     -0.00018410109922      n
    4.71469671365625      3.23469350004797     -0.00017883072891      c
    5.44971686449833      0.58008987825655      0.00034060045185      c
    3.52841441539193     -1.30941375445507     -0.00030929530672      c
    0.87840750587983     -0.57880865938216     -0.00002191196455      c
    0.30579085155969      2.06798123767513     -0.00064491894159      c
    2.14421975449051      3.92109713362541     -0.00043788352403      c
    8.00421272143430     -0.19184799820432      0.00092871504164      c
    4.21720834365952     -3.87989776614867     -0.00006215917872      c
   -0.93533792512793     -2.32747866026992     -0.00101155697276      n
    1.58084465929573      5.90456366895882     -0.00081023840135      h
    5.98155644603358      6.91729640979627     -0.00052892988122      h
    8.35538247342193      4.67262534658663     -0.00001715895372      h
    8.64425223638350     -2.73372771557460      0.00111938615815      c
    6.74158688615329     -4.58480316774273      0.00060222942173      c
    9.53769377326859      1.18783488956377      0.00132662149696      h
   10.62882887768949     -3.29010535451559      0.00168533682533      h
    7.25122070079245     -6.58243544764453      0.00079245510036      h
    2.71864142388389     -5.29287999258839     -0.00043521082096      h
   -3.36325340021570     -1.55733381113444     -0.00134223917153      c
   -5.37314641475407     -3.34463612219682     -0.00102401507747      c
   -7.84335588090102     -2.56374010625289     -0.00051786508202      c
   -8.46717695799320      0.07203456892136      0.00076554899631      c
   -6.50824708500189      1.88967814478833      0.00007017076231      c
   -4.03707582922996      1.06171531105767      0.00002039403573      c
   -4.87758668528779     -5.34499146846703     -0.00180618622914      h
   -9.36983439483192     -3.95125934446337     -0.00028980800904      h
  -10.92065386924768      0.79147844378975      0.00207070077491      n
   -6.91804835343827      3.91009185612570      0.00082974400210      h
   -2.15099247030053      2.83535835130730     -0.00060152783444      o
  -11.42437847373042      2.63985762408323      0.00281931392095      h
  -12.33142262022795     -0.50461422153558      0.00206937720623      h
$end
```

RI-PBE/TZVP optimized structure of 6,6'-difluoro-indigo (**3**)

```
$coord
    2.80305031849428      2.73387057781318      0.00000000000000      c
    1.35368136507302      0.15470827963369      0.00000000000000      c
    2.90682245934818     -1.76423981815936      0.00000000000000      n
```

```
    5.40589021679978      -0.77632668388430       0.00000000000000      c
    5.47623044914895       1.88148108497219       0.00000000000000      c
    7.75243995628494       3.18516197580274       0.00000000000000      c
   10.00504606793493       1.78475810616407       0.00000000000000      c
    9.87692910056042      -0.85073403415211       0.00000000000000      c
    7.60317636459244      -2.21090522824228       0.00000000000000      c
   -1.35368136507302      -0.15470827963369       0.00000000000000      c
   -2.90682245934818       1.76423981815936       0.00000000000000      n
   -5.40589021679978       0.77632668388430       0.00000000000000      c
   -5.47623044914895      -1.88148108497219       0.00000000000000      c
   -2.80305031849428      -2.73387057781318       0.00000000000000      c
   -7.75243995628494      -3.18516197580274       0.00000000000000      c
  -10.00504606793493      -1.78475810616407       0.00000000000000      c
   -9.87692910056042       0.85073403415211       0.00000000000000      c
   -7.60317636459244       2.21090522824228       0.00000000000000      c
  -12.06656173340738       2.16998278553654       0.00000000000000      f
   -1.95654761617987      -4.86550147051408       0.00000000000000      o
   12.06656173340738      -2.16998278553655       0.00000000000000      f
    1.95654761617987       4.86550147051408       0.00000000000000      o
   -7.57983800056685       4.27061148671628       0.00000000000000      h
  -11.85062699777944      -2.70007572007877       0.00000000000000      h
   -7.79089549794873      -5.24835374960916       0.00000000000000      h
    7.57983800056685      -4.27061148671629       0.00000000000000      h
   11.85062699777944       2.70007572007877       0.00000000000000      h
    7.79089549794873       5.24835374960916       0.00000000000000      h
$end
```

RI-PBE/TZVP optimized structure of (*E*)-(2-phenylazo-phenyl)bis(pentafluoro-phenyl)borane (**4**)

```
$coord
   -1.02399222185099       4.93567143452011       8.09588190510166      c
   -1.21780738944468       2.28947501221068       8.26342720419553      c
   -0.93087841861627       0.73411675251576       6.13634122294932      c
   -0.39782807802520       1.82040741166886       3.79865106972662      c
   -0.22566763242552       4.48828520128147       3.67817877571723      c
   -0.52664880597917       6.07847071850455       5.78158602377421      c
   -0.06846026102877       0.79357777784018       0.95465339240917      b
    0.31795459702810       5.41253595900533       1.28963052639141      n
    0.42273784260408       3.57690955069461      -0.30004541085378      n
    1.11564474417259       4.14095155709506      -2.82843890599028      c
    0.84469776692889       2.26389490999388      -4.68323078811101      c
    1.50610394316699       2.80006014296531      -7.17598433612008      c
    2.44204671024830       5.18129665234991      -7.83056311551345      c
    2.71662902659465       7.04293848213147      -5.96914884745638      c
    2.06411939327073       6.53741369791348      -3.47335216924120      c
```

```
   -2.79779801473067      -0.41198625468400       0.15444882331411      c
    2.43920717282221      -0.92084691103777       0.41630467648662      c
    4.72007280703340      -0.35384472237224       1.66198639993411      c
    6.95049969682882      -1.76066875083619       1.36048652972624      c
    6.95796040665326      -3.82696462609293      -0.30428977480313      c
    4.74287352626178      -4.44370543513826      -1.62785728839815      c
    2.55806398552288      -2.97925033788933      -1.26083518936287      c
   -3.44288449548374      -2.80619765935753       1.11515535638100      c
   -5.77445873348693      -3.98474295957977       0.67585307189950      c
   -7.62819639523052      -2.69569005787895      -0.72328482817254      c
   -7.09147208589486      -0.28357307116383      -1.68252459848391      c
   -4.72347979801095       0.82244681276133      -1.19130808046532      c
    4.85334168032036       1.65469266750801       3.22590823621811      f
    9.05898281587290      -1.13378824047401       2.60330331469155      f
    9.05533921092091      -5.18811150630122      -0.63276454830656      f
    4.73616072162524      -6.39508358926938      -3.23307944588988      f
    0.52273657211452      -3.65333089687710      -2.65106517142891      f
   -1.74349950346004      -4.10361154631328       2.51648220083203      f
   -4.38195740366062       3.18282635179142      -2.10080962378557      f
   -8.84696909601963       0.96821246776465      -3.00081406106574      f
   -9.87215590125430      -3.76688068108238      -1.15007776815550      f
   -6.26453473914806      -6.28379597209698       1.60232287043075      f
   -1.26699704727940       6.08860826492518       9.78778914986409      h
   -1.60097653193275       1.42887553108494      10.10021503953498      h
   -1.12396249817683      -1.31125939108506       6.32025705556859      h
   -0.37779545888124       8.12469174242964       5.57652714627645      h
    0.11385471799403       0.40511656351220      -4.18999104346497      h
    1.28609052733833       1.34101330743442      -8.61612866060838      h
    2.96358250890829       5.58730487004231      -9.78412842406357      h
    3.45849068451017       8.90167654067216      -6.46727806809265      h
    2.27327088858841       7.96351041529203      -2.00424937005804      h
$end
```

RI-PBE/TZVP optimized structure of the perylene-3,4,9,10-tetracarboxylic bisimide (**5**)

```
$coord
    0.00000000000000       0.00000000000000     -13.52999711477639      c
   -2.29278640965126       0.00000000000000     -14.83045886303911      c
   -2.28738517555910       0.00000000000000     -17.46881791506840      c
    0.00000000000000       0.00000000000000     -18.78915130254424      c
    2.28738517555910       0.00000000000000     -17.46881791506840      c
    2.29278640965126       0.00000000000000     -14.83045886303911      c
   -4.06477031264146       0.00000000000000     -13.77627582738347      h
   -4.07673711009647       0.00000000000000     -18.49457118238795      h
    0.00000000000000       0.00000000000000     -20.85191458122839      h
```

2 GROUND STATE GEOMETRIES OF THE ORGANIC DYE BENCHMARK SET

4.07673711009647	0.00000000000000	-18.49457118238795	h
4.06477031264146	0.00000000000000	-13.77627582738347	h
0.00000000000000	0.00000000000000	-10.79107430308213	n
0.00000000000000	-2.37560597726343	-9.56504945553020	c
0.00000000000000	2.37560597726343	-9.56504945553020	c
0.00000000000000	-2.31781156263666	-6.76141403548590	c
0.00000000000000	0.00000000000000	-5.41756576971729	c
0.00000000000000	0.00000000000000	-2.70722979514586	c
0.00000000000000	-2.36077181180116	-1.38560593704135	c
0.00000000000000	-4.60019589743217	-2.79923802604705	c
0.00000000000000	-4.58598116560458	-5.43908797024770	c
0.00000000000000	2.31781156263666	-6.76141403548590	c
0.00000000000000	2.36077181180116	-1.38560593704135	c
0.00000000000000	-2.36077181180116	1.38560593704135	c
0.00000000000000	-6.42398846574838	-1.84430967702928	h
0.00000000000000	-6.34814375021264	-6.50969412612313	h
0.00000000000000	-4.34556110374009	-10.78281924096273	o
0.00000000000000	4.34556110374009	-10.78281924096273	o
0.00000000000000	4.60019589743217	-2.79923802604705	c
0.00000000000000	4.58598116560458	-5.43908797024770	c
0.00000000000000	6.34814375021264	-6.50969412612313	h
0.00000000000000	6.42398846574838	-1.84430967702928	h
0.00000000000000	-4.60019589743217	2.79923802604705	c
0.00000000000000	-4.58598116560458	5.43908797024770	c
0.00000000000000	-2.31781156263666	6.76141403548590	c
0.00000000000000	0.00000000000000	5.41756576971729	c
0.00000000000000	0.00000000000000	2.70722979514586	c
0.00000000000000	-6.42398846574838	1.84430967702928	h
0.00000000000000	-6.34814375021264	6.50969412612313	h
0.00000000000000	-2.37560597726343	9.56504945553020	c
0.00000000000000	2.31781156263666	6.76141403548590	c
0.00000000000000	2.36077181180116	1.38560593704135	c
0.00000000000000	4.58598116560458	5.43908797024770	c
0.00000000000000	4.60019589743217	2.79923802604705	c
0.00000000000000	6.42398846574838	1.84430967702928	h
0.00000000000000	6.34814375021264	6.50969412612313	h
0.00000000000000	2.37560597726343	9.56504945553020	c
0.00000000000000	0.00000000000000	10.79107430308213	n
0.00000000000000	4.34556110374009	10.78281924096273	o
0.00000000000000	-4.34556110374009	10.78281924096273	o
0.00000000000000	0.00000000000000	13.52999711477639	c
-2.29278640965126	0.00000000000000	14.83045886303911	c
-2.28738517555910	0.00000000000000	17.46881791506840	c
0.00000000000000	0.00000000000000	18.78915130254424	c
2.28738517555910	0.00000000000000	17.46881791506840	c

```
    2.29278640965126      0.00000000000000      14.83045886303911      c
   -4.06477031264146      0.00000000000000      13.77627582738347      h
   -4.07673711009647      0.00000000000000      18.49457118238795      h
    0.00000000000000      0.00000000000000      20.85191458122839      h
    4.07673711009647      0.00000000000000      18.49457118238795      h
    4.06477031264146      0.00000000000000      13.77627582738347      h
$end
```