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Supporting Information

Distortion-Controlled Redshift of Organic Dye Molecules

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S1. Benchmark Calculations

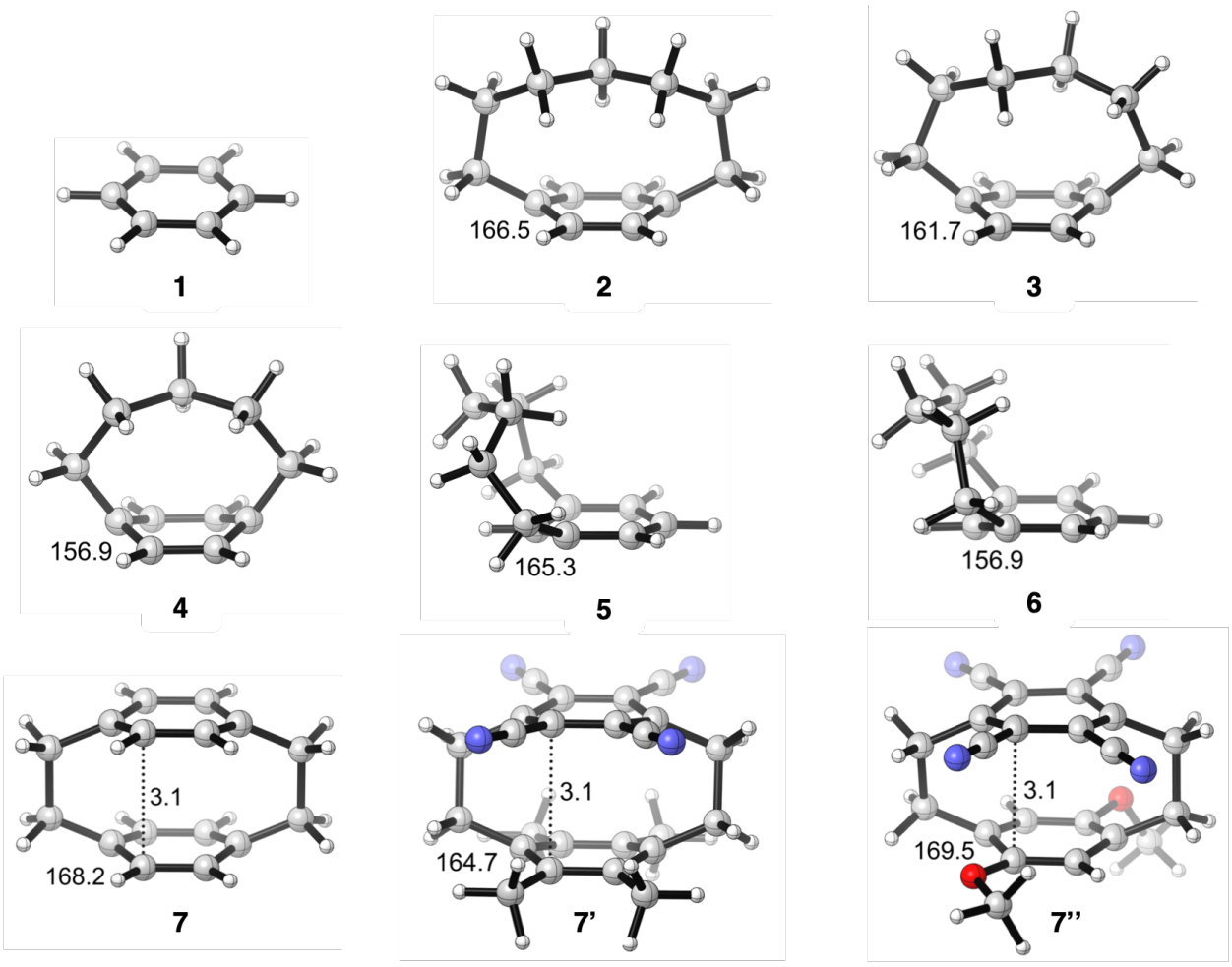

Figure S1 Benchmark molecules (**1**–**7**, **7'** and **7''**, out-of-plane bending, α, in ° and inter-core distance, d, in Å).

We have benchmarked the hybrid PBE0,[1] the meta-hybrid M06-2X[2] and the range-separated hybrid (RSH) functional CAMY-B3LYP[3] on the **1**–**7"** (see Fig. S1) geometries optimized in vacuum at BLYP-D3(BJ)/TZ2P, with a small frozen core against experimentally obtained absorption maximum in their respective solvents (Table 1). We note that there is no theoretical counterpart of the experimental λ_{max} and for an extensive benchmark one should compare the experimental vibronic spectra with the computed 0-0 transition energy.[4] However, such an extensive benchmark falls beyond the scope of our study and therefore proceeded with the comparison of the computed vertical excitation energy to experimental λ_{max}. All the functionals

exhibit overestimated excitation energies which is a good sign for the level of theory being used for the benchmark.[4a] The lowest valence ππ* excitation of benzene (**1**), which in Platt's nomenclature[5] corresponds to the L_b state, is at 4.90 eV in vacuum.[6] Our TD-DFT computations overestimate this value by >0.50 eV (Table S1). The overestimation is, in fact, a limitation of single-reference methods like TD-DFT, which fail to describe the double excitation nature of certain electronic transitions.[7] Similar to benzene, the lowest excited state of [n]paracyclophanes (**2–4**) and [n]metacyclophanes (**5–6**) also show multiconfigurational character and are thus overestimated by conventional single-determinant based methods.[8] Furthermore, in our benchmark set, we have included molecules with donor–acceptor interactions which inherently show charge-transfer excitations along with extended π-conjugated systems for which capturing long-range effects in the excitation becomes highly critical.[9] Overall, all the three functionals perform similar in terms of accuracy, which is reflected by their fairly similar MAD of ~ 0.4 eV. The computed R^2 values indicates an excellent correlation for CAMY-B3LYP (0.99) and M06-2X (0.98), while both show a better correlation than PBE0 (0.97).

Table S1 Benchmark of TD-DFT functionals to predict $E_0(S_1)$ (in eV) in bent benzene systems.[a]

Model Molecule	**Experimental λ_{max}**	**PBE0**	**M06-2X**	**CAMY-B3LYP**	**Reference**
1	4.90[b]	5.48	5.41	5.46	5
2	4.39[c]	4.90	4.86	4.90	9
3	4.18[d]	4.67	4.62	4.68	10
4	3.75[e]	4.33	4.16	4.35	11
5	4.42[e]	4.94	4.91	4.95	12
6	4.05[d]	4.52	4.47	4.53	13
7	4.10[d]	4.32	4.42	4.42	14
7'	2.82[f]	2.27	2.91	2.63	15
7''	2.38[f]	2.04	2.74	2.44	15
MD (eV)	0.00	0.28	0.37	0.39	-
MAD (eV)	0.00	0.47	0.42	0.39	-
R^2	-	0.97	0.98	0.99	-

[a] All the TDDFT calculations have been performed in their respective solvent using the TZ2P basis set on BLYP-D3(BJ)/TZ2P optimized geometries. $E_0(S_1)$ transition measured in the [b] vacuum, [c] ethanol, [d] cyclohexane, [e] n-hexane, and [f] chloroform.

Table S2. Vertical excitation energies along with the corresponding orbital composition of the first and second lowest singlet excitation computed at TD-DFT/CAMY-B3LYP for the model molecules (**1**–**15**).

Model molecule	$E_0(S_1)$	$E_0(S_2)$	MO composition of $E_0(S_1)$ (%)	MO composition of $E_0(S_2)$ (%)
1	5.46	6.18	H–1→L (50); H→L+1 (50)	H→L (50); H–1→L+1 (50)
2	4.91	5.36	H–1→L (64); H→L+1 (33)	H→L (89)
3	4.69	4.98	H–1→L (66); H→L+1 (31)	H→L (93)
4	4.38	4.42	H–1→L (70); H→L+1 (28)	H→L (96)
5	4.96	5.65	H→L (68)	H–1→L (59); H→L+1 (38)
6	4.55	5.34	H→L (78)	H–1→L (62); H→L+1 (37)
7	4.41	4.83	H→L (75)	H–1→L (62); H→L+1 (37)
8	2.96	3.37	H→L (99)	H–1→L (73); H→L+1 (25)
9	4.06	4.20	H–1→L (61); H→L+1 (27)	H→L (95)
10	2.77	3.39	H→L (94)	H–1→L (59); H→L+1 (34)
11	1.98	2.99	H→L (99)	H–1→L (96); H→L+1 (3)
12	1.70	1.85	H→L (97)	H–1→L (98)
13	1.62	2.09	H→L (84)	H–1→L (84)
14	1.60	1.75	H→L (96)	H–1→L (96)
15	1.45	1.54	H→L (98)	H–1→L (98)

The Franck-Condon absorption is associated with the vertical excitation from the occupied ϕ_i to the unoccupied ϕ_a orbital, and thus, their energy difference, $\varepsilon_a - \varepsilon_i$. Generally, it has been observed that the $\Delta E_{H\text{-}L}$ shows an outstanding linear correlation with the lowest allowed excitation energy derived from the far more accurate TD-DFT, and indeed, we have the same observation. The reason for this behavior is that most $S_1 \leftarrow S_0$ ($S_2 \leftarrow S_0$ in benzene (**1**), [n]paracyclophanes (**2–4**) and [1,1]metacyclophane (**9**)) excitations are predominantly single-electron HOMO → LUMO transitions (see Table S2). Considering the $S_1 \leftarrow S_0$ excitation ($S_2 \leftarrow S_0$ in benzene, [n]paracyclophanes and [1,1]metacyclophane), we found an excellent correlation of 0.99 (Figure S2) with the $\Delta E_{H\text{-}L}$.

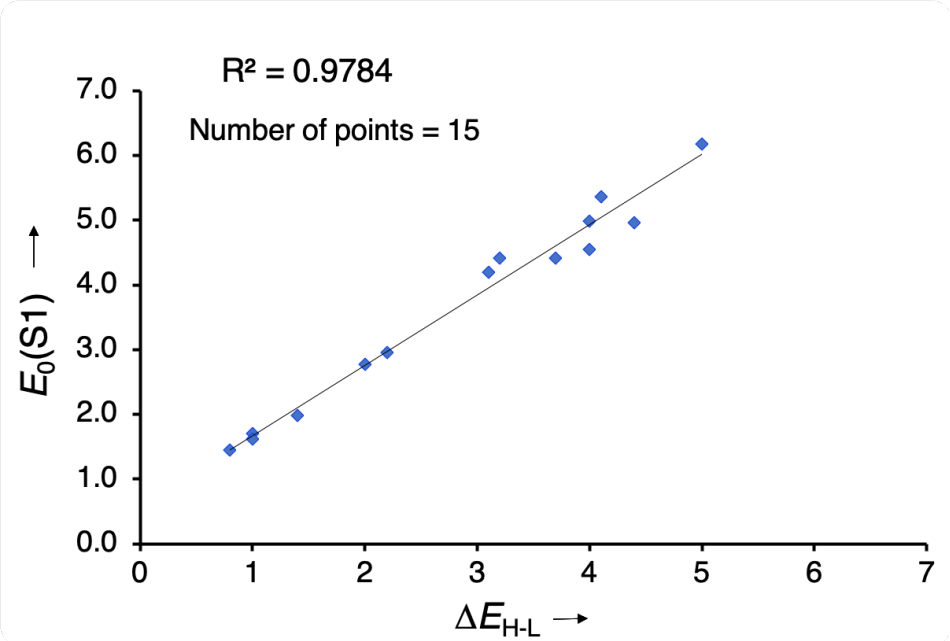

Figure S2. Correlation diagram between $E_0(S_1)$ ($E_0(S_2)$ in case of **1–4**, **9**) and $\Delta E_{H\text{-}L}$ in model systems, **1**–**15**. All energies in eV.

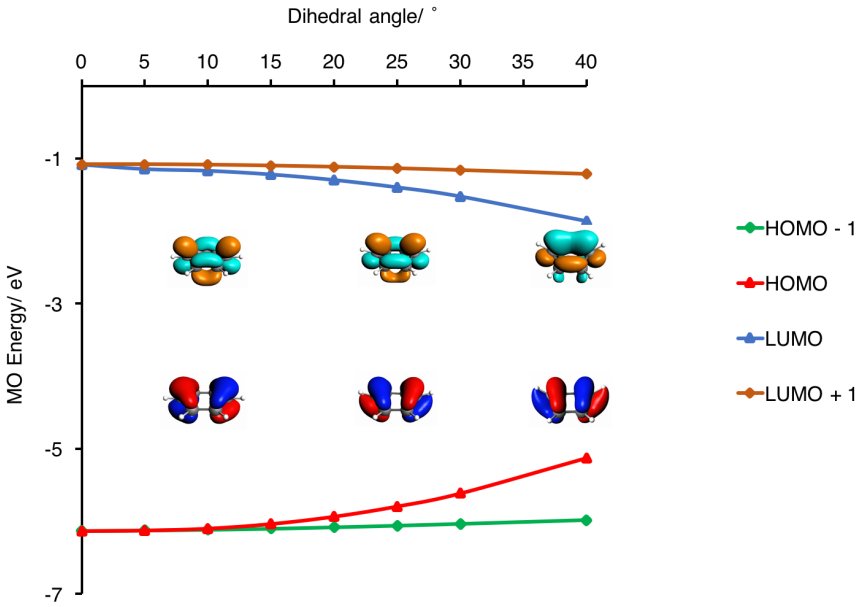

Figure S3. Radial orbital-energy slopes (ROS) of the frontier MOs of model out-of-plane bent benzene at different out-of-plane bending angles (α) computed at CAMY-B3LYP/TZ2P//BLYP-D3(BJ)/TZ2P.

Table S3. Electrostatic energy (ΔV_{elstat} in kcal mol^{-1}), π-HOMO FMOs overlap ($S_{\pi\text{-}\pi}$) and π*-LUMO FMO overlap ($S'_{\pi\text{-}\pi}$) obtained from the interaction between two equivalent C_3H_3 tri-radical fragments at different out-of-plane bending angles (α) computed at BLYP-D3(BJ)/TZ2P level of theory.

α	ΔV_{elstat}	$S_{\pi\text{-}\pi}$	$S'_{\pi\text{-}\pi}$
0°	–356.8	0.17	0.26
25°	–363.9	0.20	0.23
40°	–375.2	0.25	0.21

Table S4 Fock matrix elements and FMO energies (in eV) of an out-of-plane bent benzene model.

α	$\langle 1B_1 \lvert \widehat{F_{\rho A+\rho B}} \rvert 1B_1 \rangle$[a]	$\langle 1B_1 \lvert \widehat{F_{\rho A+\rho B}} \rvert 1B_1 \rangle$[b]	$1B_1$[c]	$\langle 2B_1 \lvert \widehat{F_{\rho A+\rho B}} \rvert 2B_1 \rangle$[a]	$\langle 2B_1 \lvert \widehat{F_{\rho A+\rho B}} \rvert 2B_1 \rangle$[b]	$2B_1$[c]
0°	–7.92	–7.55	–8.05	–0.93	–0.50	–0.50
25°	–8.65	–8.23	–8.05	–1.86	–1.40	–0.50

[a] Fock matrix element calculated before SCF. [b] Fock matrix element calculated after SCF. [c] Isolated FMO energy.

Table S5. Changes in absorption properties upon change in out-of-plane bending angle α.Orbital energy (H = HOMO, L = LUMO) and gap ΔE_{H-L}, lowest singlet excitation energy $E_0(S_1)$ and the corresponding MO composition and oscillator strength f.[a]

α	H[b]	L[b]	H–L gap (ΔE_{H-L})[b]	$E_0(S_1)$[c]	MO composition of S_1 ← S_0 (%)	Osc. Strength, f[c]
0	–8.2	0.6	8.8	5.46 (B_{2u})	$1e_{1g}$(H, H–1) → $1e_{2u}$ (L+1, L) (100)	0.000
5	–8.2	0.5	8.7	5.38 (B_1)	$6b_2$(H) → $4a_2$(L+1) (48); $5b_1$(H–1) → $8a_1$(L) (52)	0.000
10	–8.1	0.5	8.6	5.35 (B_1)	$6b_2$(H) → $4a_2$(L+1) (47); $5b_1$(H–1) → $8a_1$(L) (52)	0.000
15	–8.1	0.4	8.5	5.27 (B_1)	$6b_2$(H) → $4a_2$(L+1) (58); $5b_1$(H–1) → $8a_1$(L) (42)	0.000
20	–8.0	0.3	8.3	5.16 (B_1)	$6b_2$(H) → $4a_2$(L+1) (47); $5b_1$(H–1) → $8a_1$(L) (52)	0.000
25	–7.8	0.2	8.0	5.01 (B_1)	$6b_2$(H) → $4a_2$(L+1) (47); $5b_1$(H–1) → $8a_1$(L) (51)	0.000
30	–7.7	0.1	7.8	4.83 (B_1)	$6b_2$(H) → $4a_2$(L+1) (49); $5b_1$(H–1) → $8a_1$(L) (50)	0.000
35	–7.4	–0.1	7.3	4.60 (B_1)	$6b_2$(H) → $4a_2$(L+1) (52); $5b_1$(H–1) → $8a_1$(L) (48)	0.001
40	–7.2	–0.3	6.9	4.29 (B_2)	$6b_2$(H) → $8a_1$(L) (98)	0.040

Table S6. Orbital energy (H = HOMO, L = LUMO) and gap $\Delta E_{H–L}$, first singlet excitation energy $E_0(S_1)$ and the corresponding MO composition and oscillator strength f for the model benzene systems.[a]

β	H[b]	L[b]	H–L gap (ΔE_{H-L})[b]	$E_0(S_1)$[c]	MO composition of S_1 ← S_0 (%)	Osc. Strength, f[c]
0	–7.7	0.2	7.9	4.93 (B_1)	$6b_2$(H) → $4a_2$(L+1) (51); $5b_1$(H–1) → $8a_1$(L) (48)	0.000
5	–7.7	0.1	7.8	4.86 (B_1)	$6b_2$(H) → $4a_2$(L+1) (54); $5b_1$(H–1) → $8a_1$(L) (45)	0.000
10	–7.6	0.0	7.6	4.77 (B_1)	$6b_2$(H) → $4a_2$(L+1) (56); $5b_1$(H–1) → $8a_1$(L) (43)	0.000
15	–7.5	–0.1	7.4	4.67 (B_1)	$6b_2$(H) → $4a_2$(L+1) (58); $5b_1$(H–1) → $8a_1$(L) (42)	0.000
20	–7.4	–0.2	7.2	4.56 (B_1)	$6b_2$(H) → $4a_2$(L+1) (59); $5b_1$(H–1) → $8a_1$(L) (40)	0.002
25	–7.3	–0.3	7.0	4.45 (B_1)	$6b_2$(H) → $4a_2$(L+1) (60); $5b_1$(H–1) → $8a_1$(L) (39)	0.002
30	–7.2	–0.5	6.7	4.34 (B_1)	$6b_2$(H) → $4a_2$(L+1) (62); $5b_1$(H–1) → $8a_1$(L) (38)	0.002
35	–7.2	–0.6	6.6	4.22 (B_1)	$6b_2$(H) → $4a_2$(L+1) (63); $5b_1$(H–1) → $8a_1$(L) (37)	0.002
40	–7.1	–0.8	6.3	4.07 (B_2)	$6b_2$(H) → $8a_1$(L) (96)	0.090

For all the MO diagrams below, Figures S4-S8, the overlap between the FMOs involved in the formation of the overall MO has been denoted by *S* and enclosed in parentheses. The color of the MO signifies which FMO contributes more towards the formation of that MO in terms of Gross Mulliken contribution. $\Delta E_{H\text{-}L}$ is the HOMO–LUMO gap of the whole system denoted in brown. The diagrams are not to scale but they do show the correct relative orbital energy ordering of fragment MOs (FMOs) and overall MOs.

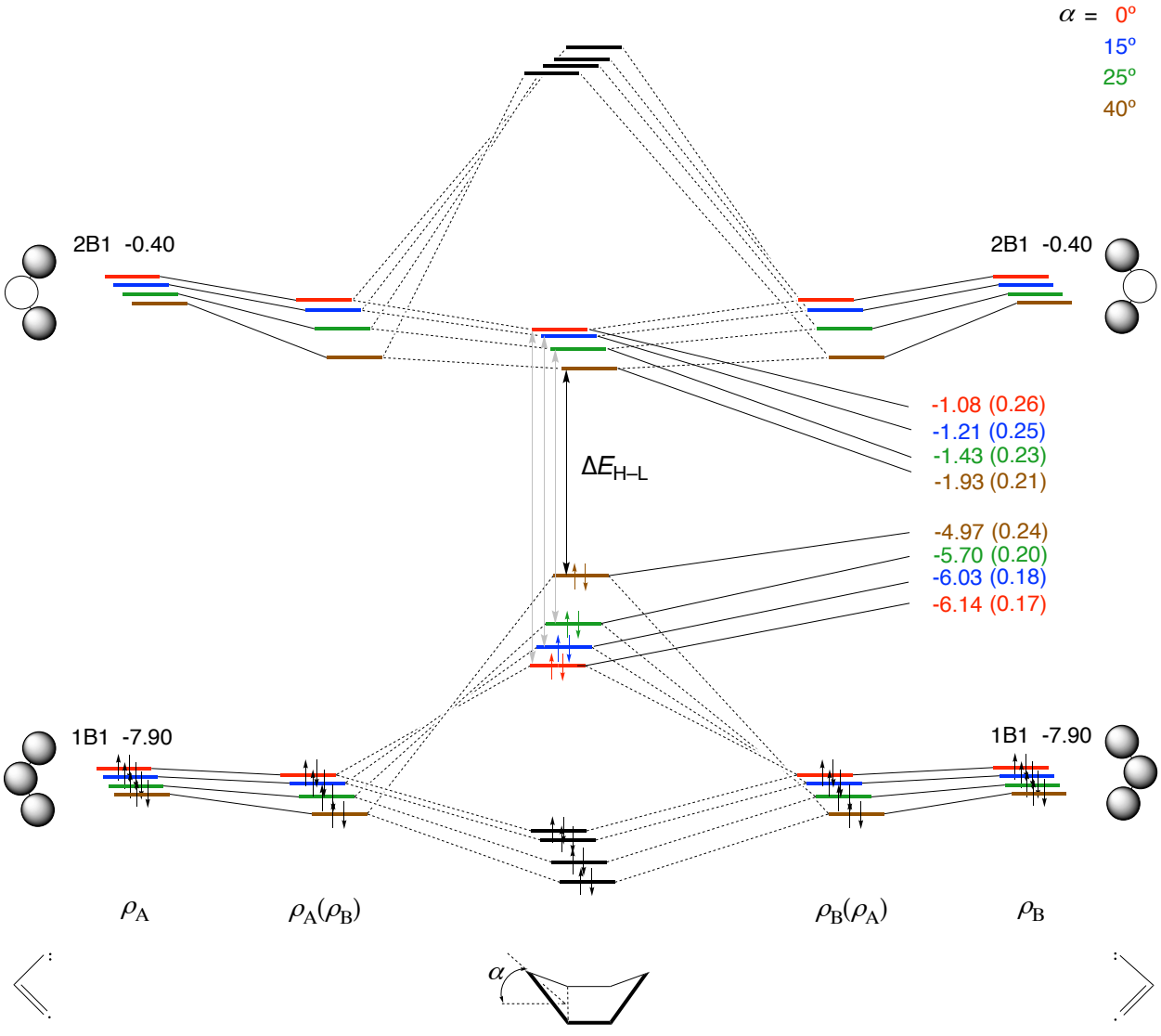

Figure S4. π-FMO interaction diagram based on quantitative KS-MO analysis depicting the effect of out-of-plane bending (α) on $\Delta E_{H\text{-}L}$ computed at BLYP-D3(BJ)/TZ2P. Both the fragments are triradical and exhibits a quartet electronic configuration Overlaps (*S*) between the π-FMO are mentioned in parentheses. All the energies are in eV unless stated otherwise.

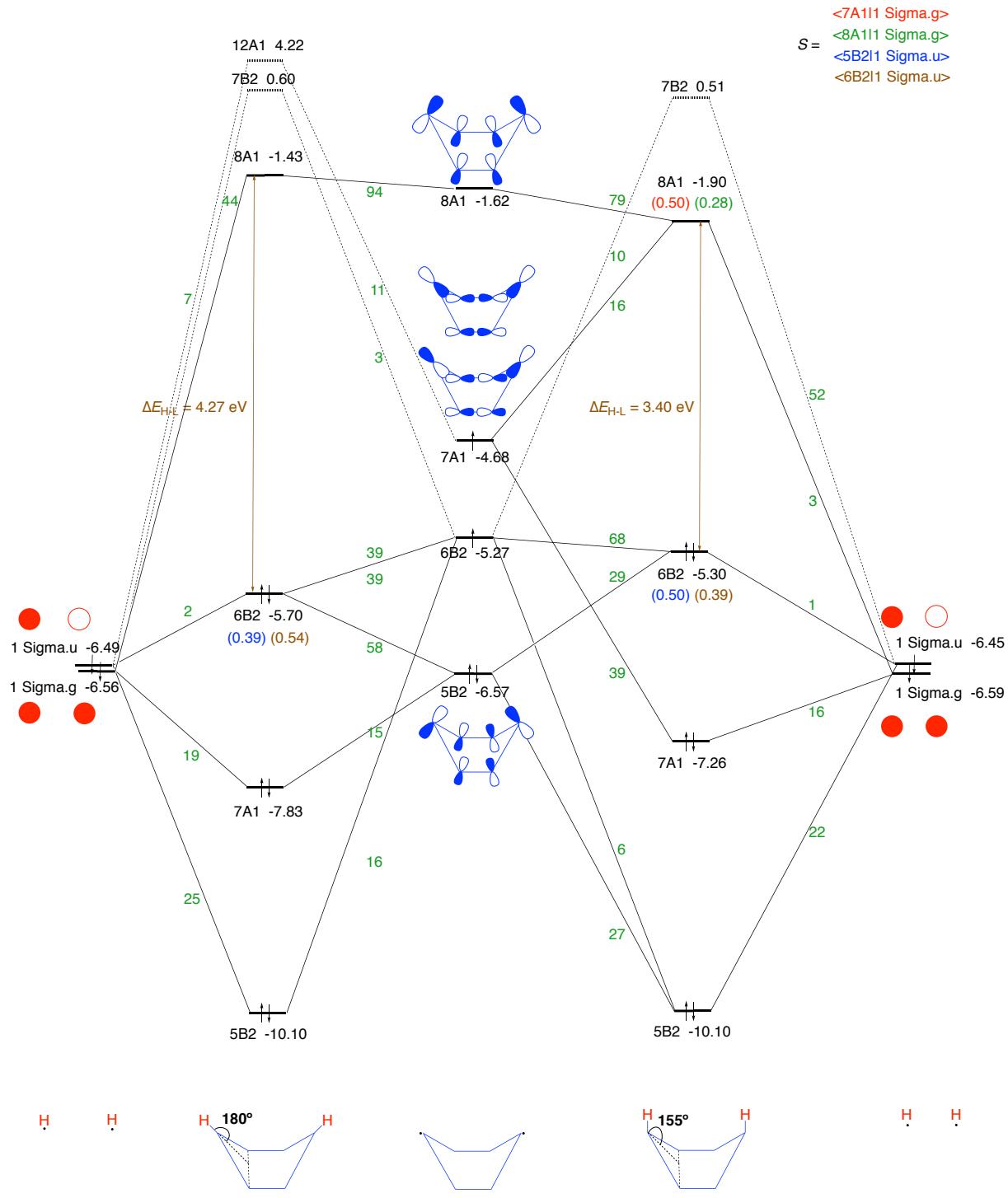

Figure S5. FMO interaction diagram based on quantitative KS-MO analysis depicting the effect of bending the bridge (β) on $\Delta E_{H\text{-}L}$ computed at BLYP-D3(BJ)/TZ2P. Both the fragments are diradical and exhibits a triplet electronic configuration Overlaps (S) between the FMOs of the two fragments are mentioned in parentheses. Contribution of the FMO to the overall MO is represented in green. All the energies are in eV unless stated otherwise.

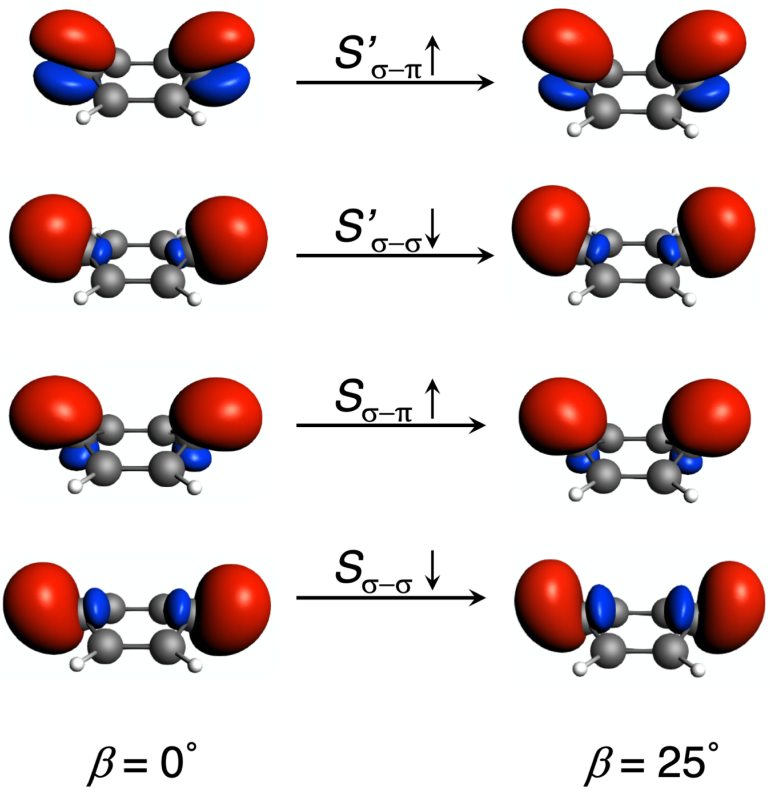

Figure S6. Overlap density between the σ and π FMOs of [H---H]¨ and [C_6H_4]¨ forming the overall C_6H_6 for β = 0º and β = 25º (isovalue = ±0.002 au). Red and blue isosurfaces indicate positive and negative phase, respectively.

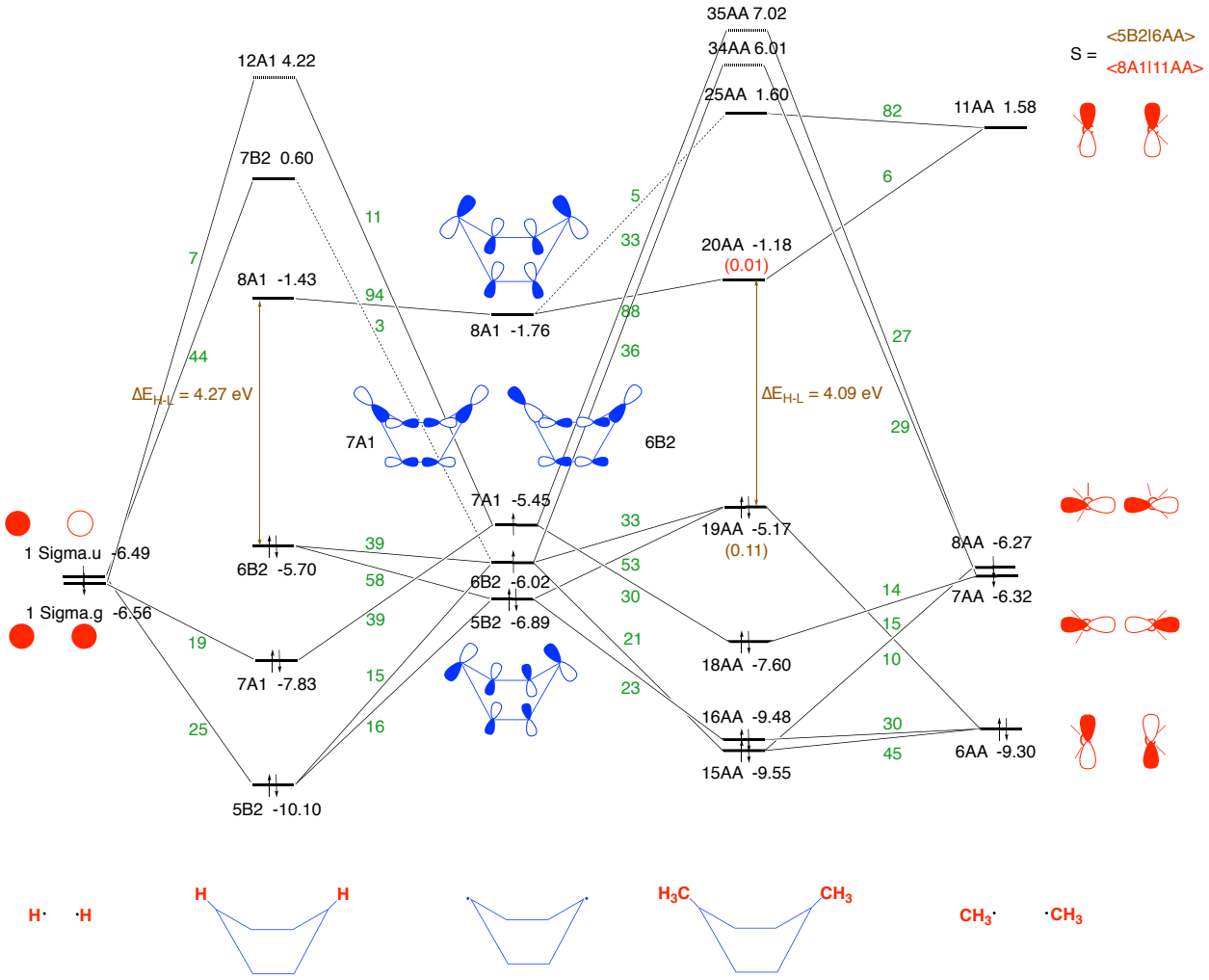

Figure S7 FMO interaction diagram based on quantitative KS-MO analysis depicting the effect of the chemical nature of bridge (X) on $\Delta E_{H\text{-}L}$ computed at BLYP-D3(BJ)/TZ2P. Both the fragments are diradical and exhibits a triplet electronic configuration. Overlaps (S) between the FMOs of the two fragments are mentioned in parentheses. Contribution of the FMO to the overall MO is represented in green. All the energies are in eV unless stated otherwise.

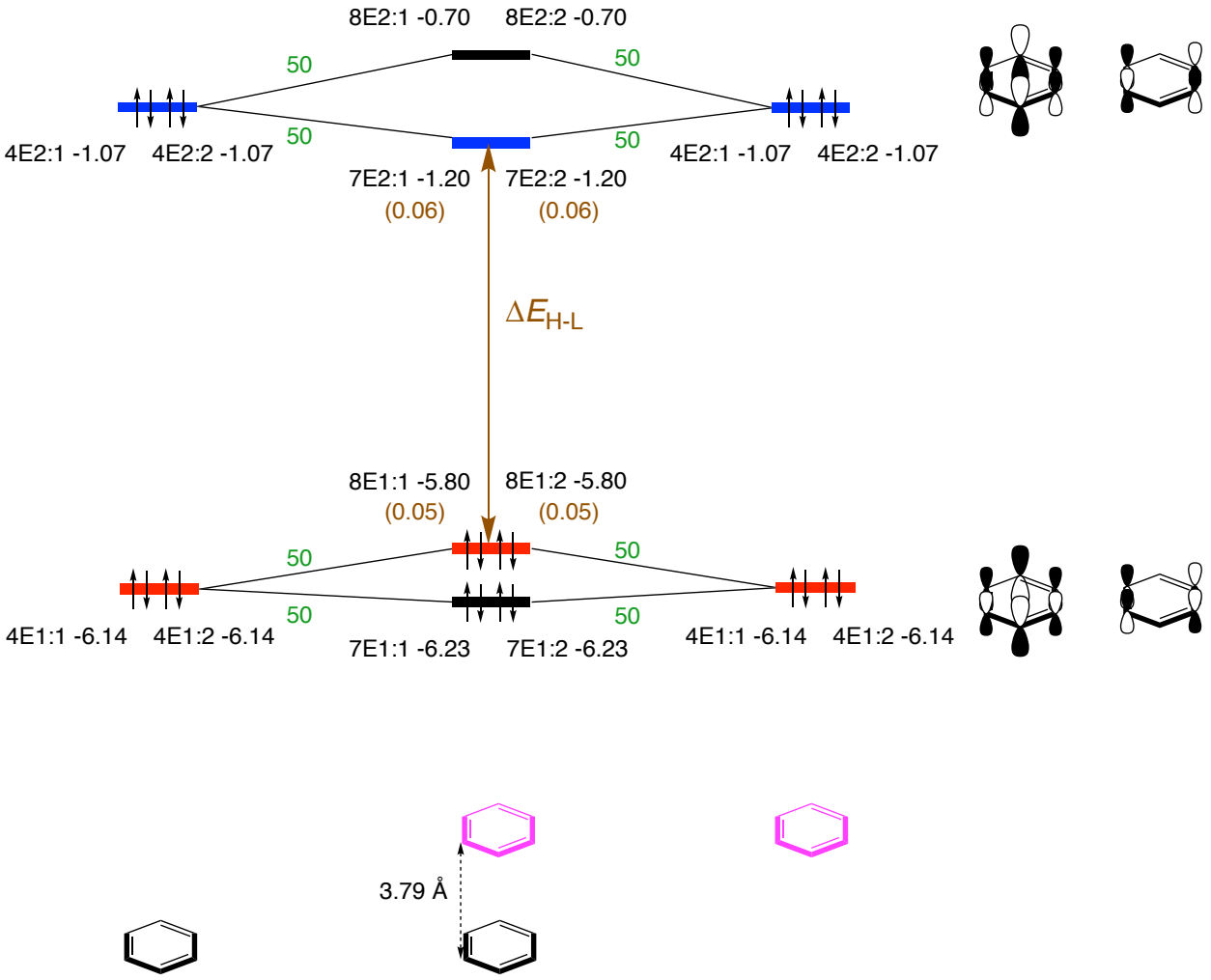

Figure S8. π-FMO interaction diagram based on quantitative KS-MO analysis depicting the effect of stacking on $\Delta E_{H\text{-}L}$ computed at BLYP-D3(BJ)/TZ2P. Both the fragments are closed-shell and exhibits a singlet electronic configuration Overlaps (*S*) between the FMOs of the two fragments are mentioned in parentheses. Contribution of the FMO to the overall MO is represented in green. All the energies are in eV unless stated otherwise.

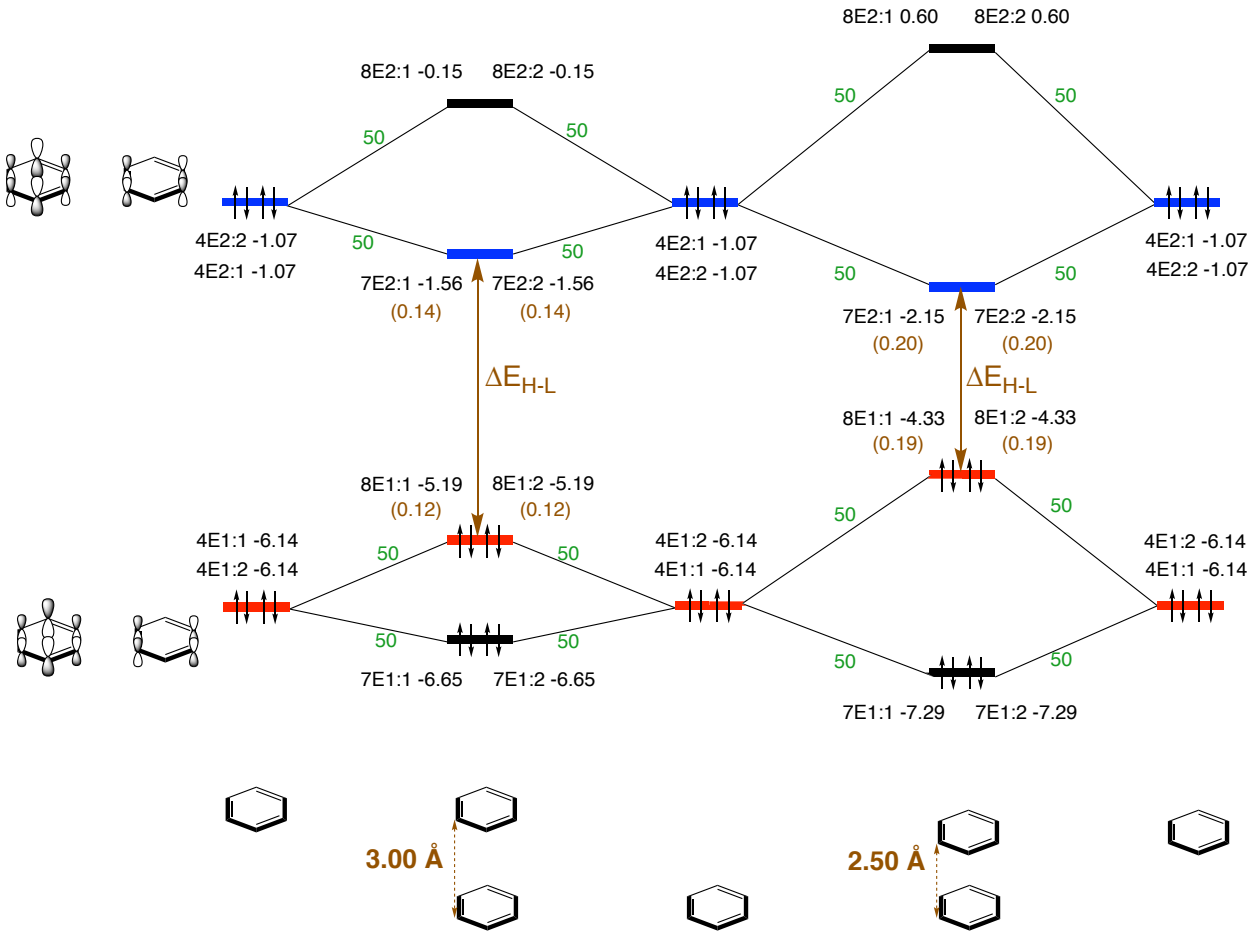

Figure S9. π-FMO interaction diagram based on quantitative KS-MO analysis depicting the effect of inter-core distance (*d*) on $\Delta E_{H\text{-}L}$ computed at BLYP-D3(BJ)/TZ2P. Both the fragments are closed-shell and exhibits a singlet electronic configuration Overlaps (*S*) between the FMOs of the two fragments are mentioned in parentheses. Contribution of the FMO to the overall MO is represented in green. All the energies are in eV unless stated otherwise.

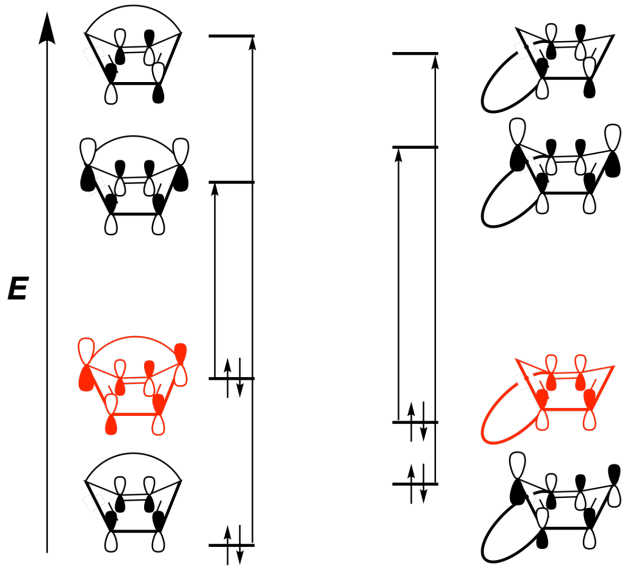

Figure S10. Schematic π-valence electronic structure of model systems **4** (left) and **6** (right). The single headed-arrows represent the nature of the $S_1 \leftarrow S_0$ transition. The pentamethylene bridge has been denoted by a curved line.

$$\lambda = \frac{\sum_{i,a} K_{i,a}^2 \langle |\psi_a||\psi_i| \rangle}{\sum_{i,a} K_{i,a}^2} \quad (1)$$

Here ψ_a and ψ_i are the virtual and occupied MO participating in the electronic transition and $K_{i,a}$ is the contribution of the occupied-virtual pair to the corresponding electronic transition.

Table 4. Tozer's index for the $S_1 \leftarrow S_0$ excitation, i.e., the spatial overlap between the modulus of the participating orbitals. See Eq. 1.

Compound	Tozer's index, λ
17	0.57
18	0.78

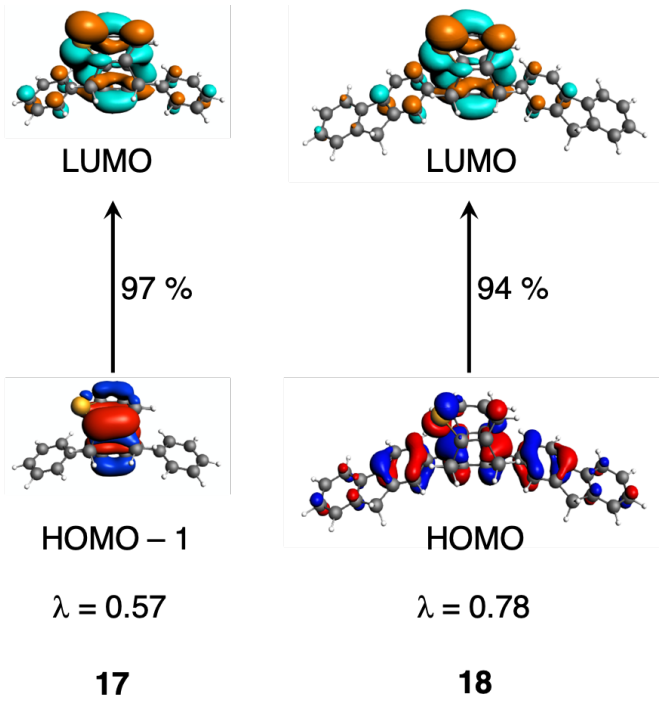

Figure S11. MO composition of the $S_1 \leftarrow S_0$ excitation along with the corresponding spatial overlap determined by Tozer's index. See Eq. 1.

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Table S5. Cartesian coordinates (in Å) of stationary points, ADF total energy (E_{tot} in Hartree), and the number of imaginary vibrational frequencies (N_{imag}) computed at ZORA-BLYP-D3(BJ)/TZ2P in vacuum.

1

E_{tot} = –2.754

N_{imag} = 0

C	0.000000	-1.398164	0.000000
C	1.210846	-0.699082	0.000000
C	1.210846	0.699082	0.000000
C	0.000000	1.398164	0.000000
C	-1.210846	0.699082	0.000000
C	-1.210846	-0.699082	0.000000
H	2.155007	-1.244194	0.000000
H	2.155007	1.244194	0.000000
H	0.000000	2.488388	0.000000
H	-2.155007	1.244194	0.000000
H	-2.155007	-1.244194	0.000000
H	0.000000	-2.488388	0.000000

2

E_{tot} = –6.462

N_{imag} = 0

C	-2.066789	-0.274046	-0.584585
C	-2.949820	-1.317733	-0.272623
C	-2.562115	-2.330499	0.602425
C	-1.284661	-2.317261	1.180565
C	-0.319427	-1.472835	0.604576
C	-0.708191	-0.457271	-0.272855
H	-3.987736	-1.254166	-0.593785
H	-3.301377	-3.047110	0.955164
C	-2.634862	1.094797	-0.866409
H	-3.623205	0.998710	-1.333574
H	0.020745	0.288910	-0.585229
C	-2.785391	1.900920	0.481405
C	-3.345555	1.117281	1.710292
C	-2.236422	0.467037	2.587376
C	-2.604800	-0.818943	3.382818
C	-1.385504	-1.758979	3.642667
H	0.707613	-1.505414	0.964922
H	-2.002510	1.677152	-1.548601
H	-3.427805	2.765679	0.271096
H	-1.799850	2.305231	0.748881
H	-4.041250	0.343454	1.364563
H	-3.940874	1.807191	2.322482
H	-1.861467	1.221071	3.294185
H	-1.393204	0.233401	1.943317
H	-3.385166	-1.371743	2.846373
H	-3.042754	-0.539920	4.350025
H	-0.482358	-1.139443	3.725043
H	-1.506048	-2.260371	4.611614
C	-1.112898	-2.882156	2.568779
H	-1.823782	-3.703063	2.727062
H	-0.104544	-3.282024	2.735231

3

E_{tot} = –5.855

N_{imag} = 0

C	-2.077360	-0.365490	-0.749262
C	-2.884325	-1.473406	-0.437234
C	-2.462745	-2.392626	0.523450
C	-1.240023	-2.185912	1.182586
C	-0.298946	-1.351797	0.554348
C	-0.714254	-0.445326	-0.421044
H	-3.916328	-1.498603	-0.783461
H	-3.173885	-3.117289	0.917147
C	-2.720456	0.994012	-0.862185
H	-3.762115	0.903588	-1.194769
H	-0.032965	0.340215	-0.744489
C	-2.677142	1.653214	0.578077
C	-3.102155	0.752158	1.790299
C	-1.947877	0.234607	2.728664
C	-2.103773	-1.215867	3.306414
C	-1.184664	-2.345202	2.681337
H	0.702388	-1.263999	0.972910
H	-2.201339	1.663844	-1.559852
H	-3.313097	2.547376	0.545818
H	-1.652529	2.008906	0.744707
H	-3.673130	-0.102555	1.419873
H	-3.800630	1.327640	2.409810
H	-1.871669	0.928384	3.574672
H	-0.994895	0.310081	2.199643
H	-3.146063	-1.535468	3.181405
H	-1.912460	-1.201995	4.387247
H	-0.156558	-2.227046	3.045878
H	-1.555294	-3.318124	3.029057

4

E_{tot} = –5.241

N_{imag} = 0

C	-1.982192	-0.407893	-0.862296
C	-2.805714	-1.524772	-0.598100
C	-2.451182	-2.385188	0.434336
C	-1.281958	-2.107196	1.176712
C	-0.271566	-1.379473	0.529433
C	-0.628181	-0.514044	-0.508957
H	-3.820317	-1.557013	-0.993005
H	-3.194301	-3.076284	0.830003
H	-2.393720	-0.339185	3.869661
H	-0.478645	-1.665018	3.134341
H	0.070815	0.265276	-0.808664
C	-2.610795	0.958372	-0.733705
C	-3.097637	1.085766	0.777233
C	-2.135846	0.721535	1.979976
C	-2.401372	-0.603119	2.804018
C	-1.445870	-1.868845	2.658113
H	0.696194	-1.252337	1.012188
H	-1.921210	-2.699554	3.196359
H	-3.490521	1.109626	-1.373215
H	-1.885425	1.749411	-0.961608
H	-4.004547	0.476051	0.871312
H	-3.412209	2.129562	0.907060
H	-2.247839	1.539971	2.700433
H	-1.092038	0.763164	1.656057
H	-3.418688	-0.945262	2.578013

5

E_{tot} = –5.875

N_{imag} = 0

C	-2.336006	-0.626378	-0.186790
C	-1.803302	0.698382	-0.855522
C	-1.538954	-1.952755	-0.400032
C	-1.639122	1.939124	0.094757
C	-0.382661	-2.274763	0.608886
C	-0.166560	2.411192	0.403608
C	0.671086	-1.198509	0.507091
C	0.779444	1.226894	0.397098
C	0.308914	0.056504	0.995863
C	1.777492	-1.287603	-0.352677
C	1.882694	1.133824	-0.462321
C	2.425512	-0.120922	-0.774016
H	-3.344659	-0.806582	-0.579214
H	-2.475062	-0.466091	0.889973
H	-2.512560	0.974692	-1.644480
H	-0.857444	0.497215	-1.367356
H	-1.122619	-1.962203	-1.416803
H	-2.252114	-2.786737	-0.349111
H	-2.140088	1.715098	1.044671
H	-2.178393	2.796200	-0.326203
H	0.027436	-3.264034	0.370483
H	-0.799783	-2.322497	1.624057
H	-0.165696	2.946188	1.363392
H	0.161228	3.127934	-0.358830
H	-0.542328	0.120644	1.666731
H	2.087933	-2.255966	-0.740959
H	2.272642	2.029217	-0.943092
H	3.289734	-0.188089	-1.431543

6

E_{tot} = –5.269

N_{imag} = 0

C	-1.975507	-0.355685	0.583982
C	-2.088911	0.198315	-0.889214
C	-0.817256	-1.333351	1.022804
C	-1.436046	1.584837	-1.273503
C	0.512289	-0.762152	1.656978
C	1.159574	0.081969	0.582658
C	0.053674	1.414137	-1.080512
C	0.373122	1.187446	0.258305
C	2.037603	-0.423796	-0.390153
C	0.921553	0.920868	-2.068731
C	1.988886	0.089974	-1.695095
H	-2.890611	-0.947884	0.718180
H	-2.065439	0.467998	1.303664
H	-3.160702	0.277814	-1.117208
H	-1.682615	-0.558107	-1.574532
H	-0.532386	-1.942750	0.154240
H	-1.247962	-2.026376	1.758487
H	-1.844290	2.372851	-0.626746
H	-1.703300	1.822244	-2.310824
H	1.141755	-1.604940	1.968893
H	0.266991	-0.170553	2.549019
H	-0.292397	1.585391	1.019686
H	2.676576	-1.274902	-0.162002
H	0.708768	1.095997	-3.121713
H	2.682294	-0.276064	-2.449391

7

E_{tot} = –7.123

N_{imag} = 0

C	-0.008036	-1.406274	-1.415569
C	-1.224920	-1.526004	-0.726051
C	-1.254226	-1.522627	0.669251
C	-0.069336	-1.404560	1.413788
C	1.139348	-1.589355	0.724262
C	1.168791	-1.587656	-0.671021
H	-2.161753	-1.470604	-1.277760
H	-2.213533	-1.464201	1.180349
H	2.213533	1.464201	1.180349
H	2.077821	-1.584246	1.275961
H	2.129838	-1.580827	-1.182134
C	0.045789	-0.809686	-2.805387
C	-0.045789	0.809686	-2.805387
C	0.008036	1.406274	-1.415569
C	-1.168791	1.587656	-0.671021
C	-1.139348	1.589355	0.724262
C	0.069336	1.404560	1.413788
C	1.254226	1.522627	0.669251
C	1.224920	1.526004	-0.726051
H	-2.129838	1.580827	-1.182134
H	-2.077821	1.584246	1.275961
H	2.161753	1.470604	-1.277760
C	-0.090891	-0.805840	2.803622
C	0.090891	0.805840	2.803622
H	-0.775004	-1.188072	-3.424870
H	0.983287	-1.094245	-3.295085
H	0.775004	1.188072	-3.424870
H	-0.983287	1.094245	-3.295085
H	-1.043216	-1.037713	3.292505
H	0.706993	-1.229362	3.423857
H	-0.706993	1.229362	3.423857
H	1.043216	1.037713	3.292505

8

E_{tot} = –5.856

N_{imag} = 0

C	1.339687	1.259774	0.004866
C	0.631344	1.564276	1.183166
C	-0.769772	1.588487	1.160462
C	-1.449699	1.307787	-0.040272
C	-0.731298	1.589692	-1.218122
C	0.669814	1.565527	-1.195412
H	-1.274908	-1.317596	-2.187826
C	-2.469381	0.125226	-0.057406
C	1.298900	-1.139324	0.002999
C	0.580499	-1.421232	1.180848
C	-0.820613	-1.397058	1.158139
C	-1.490486	-1.091307	-0.042139
C	-0.782144	-1.395810	-1.220439
C	0.618973	-1.420017	-1.197736
H	1.145212	-1.359308	-2.148617
C	2.318582	0.043246	0.020129
H	1.124109	1.486064	2.150552
H	-1.296012	1.527776	2.111342
H	-1.226477	1.529973	-2.185600
H	1.193688	1.488392	-2.146397
H	2.938706	0.032044	0.922855
H	2.967745	0.032927	-0.861937
H	-3.089497	0.136432	-0.960139
H	-3.118561	0.135542	0.824648
H	1.075678	-1.361520	2.148325
H	-1.344485	-1.319920	2.109125

9

E_{tot} = –5.867

N_{imag} = 0

C	-1.384434	-0.193908	1.118683
C	-0.689560	1.015649	0.934098
C	0.647618	1.057499	1.357179
C	1.283398	-0.125360	1.769986
C	0.672991	-1.363299	1.507723
C	-0.664229	-1.402273	1.084438
H	1.071117	-2.481183	-1.861176
H	1.027365	1.756738	-2.124266
C	-1.538504	-0.353274	-1.418240
C	-0.835461	0.864460	-1.470992
C	0.440682	0.842882	-2.053865
C	1.030833	-0.387077	-2.389680
C	0.465656	-1.577897	-1.903564
C	-0.810440	-1.553465	-1.320687
H	2.015091	-0.405658	-2.851779
H	-2.548606	-0.339216	-1.024793
C	-1.184808	1.846001	-0.299789
H	1.231416	1.968636	1.241957
H	1.275874	-2.269282	1.505615
C	-1.140539	-2.389331	-0.036313
H	-2.434683	-0.221476	0.851245
H	2.316290	-0.093472	2.108814
H	-0.637693	2.789664	-0.392266

H	-2.259015	2.056607	-0.247849
H	-2.210127	-2.614416	0.042920
H	-0.573615	-3.325498	-0.011951

10

E_{tot} = –6.129

N_{imag} = 0

C	1.382867	1.193204	-0.011163
C	0.674971	1.728411	1.094910
C	-0.721638	1.707171	1.069092
C	-1.404347	1.302508	-0.103112
C	-0.678366	1.389324	-1.296880
C	0.722088	1.154079	-1.245785
H	-1.242870	-1.091594	-2.164795
C	-2.436977	0.114469	-0.032476
C	1.317422	-1.170482	0.054873
C	0.582753	-1.603269	1.187921
C	-0.810635	-1.506844	1.158704
C	-1.471738	-1.131035	-0.035241
C	-0.753390	-1.323866	-1.221232
C	0.657939	-1.163814	-1.181100
C	1.135356	-0.043357	-2.151084
C	2.332379	-0.009252	0.256419
H	1.176120	1.863656	2.051774
H	-1.257035	1.782515	2.013883
H	-1.181382	1.132364	-2.226818
H	-1.347925	-1.499624	2.105414
H	2.719744	0.008608	1.278313
H	3.178790	-0.052056	-0.435994
H	-3.107946	0.108927	-0.898060
H	-3.034435	0.156581	0.883755
H	1.077062	-1.712133	2.151683
H	0.592963	-0.054811	-3.098827
H	2.208720	-0.078659	-2.350599

11

E_{tot} = –6.383

N_{imag} = 0

H	1.570441	-3.127423	-2.058381
C	0.324671	-1.451707	-1.569835
C	1.273948	-2.452392	-1.256376
H	-2.049942	0.083061	-1.534803
H	-2.116533	0.140431	0.240202
C	0.745861	-2.181454	1.100366
C	-0.197345	-0.660258	-0.528466
C	0.245920	-0.893900	0.794283
C	1.267800	-2.972834	0.059088
H	-0.602544	-2.302717	2.856017
H	0.345945	-3.784701	2.606084
H	-0.260035	-0.352494	1.592846
H	-0.654817	-4.545723	-2.095904
C	-0.717514	-4.237964	0.025407
C	-1.160779	-4.004319	-1.297343
C	-0.746101	-1.934715	-2.605108
C	0.827744	-4.474457	0.114150
C	-2.182652	-1.925384	-0.562146
C	-1.239528	-3.446517	1.066777
C	-2.188801	-2.445829	0.753316
C	-1.660722	-2.716771	-1.603427
C	-1.742599	-0.423765	-0.617209
C	-0.168742	-2.963502	2.102045
H	-2.485303	-1.770800	1.555322
H	-1.260794	-1.113515	-3.109144
H	-0.312303	-2.595489	-3.359090
H	1.201685	-5.038651	-0.743258
H	1.135090	-4.981281	1.031744

12

E_{tot} = –6.209

N_{imag} = 0

H	1.622342	-3.127466	-2.088672
C	0.378916	-1.453842	-1.602931
C	1.320873	-2.455278	-1.286437
H	-1.891357	0.190082	-1.655956
H	-2.049423	0.253349	0.106299
C	0.791668	-2.191426	1.069805
C	-0.153899	-0.664995	-0.564330
C	0.261702	-0.917351	0.763052
C	1.321130	-2.974670	0.025233
H	-0.430416	-2.359745	2.903928
H	0.572760	-3.786972	2.602003
H	-0.261701	-0.387918	1.560385
H	-0.615814	-4.507792	-2.082678
C	-0.661134	-4.235087	0.034712
C	-1.138484	-3.979820	-1.287126
C	-0.671469	-1.939192	-2.639835
C	0.895570	-4.468343	0.067900
C	-2.241811	-1.807848	-0.714357
C	-1.143593	-3.580383	1.183332
Si	-2.543457	-2.467347	0.938621
C	-1.624172	-2.680866	-1.629312
C	-1.669063	-0.344119	-0.727424

C	-0.020938	-3.004245	2.120531
H	-2.973131	-1.558360	2.036285
H	-1.180277	-1.131273	-3.171374
H	-0.235120	-2.626662	-3.367867
H	1.244526	-5.014828	-0.811124
H	1.215586	-4.998088	0.968513

13

E_{tot} = –6.096

N_{imag} = 0

H	1.669033	-3.117549	-2.074685
C	0.372789	-1.499393	-1.578037
C	1.348344	-2.452065	-1.273954
H	-1.926172	0.130407	-1.634987
H	-2.103955	0.162926	0.131462
C	0.833980	-2.208139	1.094021
C	-0.185369	-0.719543	-0.529139
C	0.255456	-0.936938	0.778549
C	1.370439	-2.975373	0.054342
H	-0.457129	-2.375040	2.883771
H	0.492290	-3.844508	2.564305
H	-0.277502	-0.426690	1.580116
H	-0.623695	-4.545645	-2.136534
C	-0.629505	-4.181596	-0.036940
C	-1.115206	-3.994994	-1.336168
C	-0.667390	-1.947465	-2.644894
C	0.917781	-4.461648	0.059530
C	-2.252897	-1.884182	-0.729087
C	-1.146688	-3.472941	1.079068
P	-2.541800	-2.397203	0.990023
C	-1.645093	-2.694839	-1.671769
C	-1.708763	-0.412099	-0.710725
C	-0.040128	-3.011080	2.099329
H	1.191409	-5.009475	0.963733
H	-1.152995	-1.119945	-3.167276
H	-0.225519	-2.622466	-3.381419
H	1.283840	-5.007122	-0.812950

14

E_{tot} = –5.806

N_{imag} = 0

H	1.987283	-0.731443	-1.782153
C	0.716195	0.892962	-1.272195
C	1.696321	-0.049006	-0.985523
H	-1.611823	2.544848	-1.355118
H	-1.712645	2.631243	0.420396
C	1.375777	0.195904	1.458927
C	0.209009	1.794361	-0.285322
P	0.854909	1.939198	1.336837
C	1.772422	-0.561696	0.372853
H	-0.082351	0.142151	3.131259
H	0.746399	-1.409261	2.877539
H	1.712645	-2.631243	-0.420396
H	1.611823	-2.544848	1.355118
C	-0.209009	-1.794361	0.285322
P	-0.854909	-1.939198	-1.336837
C	-0.343956	0.524615	-2.376662
C	1.324317	-2.053878	0.421890
C	-1.772422	0.561696	-0.372853
C	-0.716195	-0.892962	1.272195
C	-1.696321	0.049006	0.985523
C	-1.375777	-0.195904	-1.458927
C	-1.324317	2.053878	-0.421890
C	0.343956	-0.524615	2.376662
H	-1.987283	0.731443	1.782153
H	-0.746399	1.409261	-2.877539
H	0.082351	-0.142151	-3.131259

15

E_{tot} = –6.707

N_{imag} = 0

N	-0.023452	1.084006	-2.830051
C	-1.282670	1.027177	-0.761594
C	-0.017705	1.193905	-1.480742
H	-3.127290	0.007375	1.117427
H	-2.024748	0.304067	2.479974
C	1.268300	1.230491	0.618633
C	-1.354669	1.280601	0.603256
P	-0.021790	1.946582	1.615357
C	1.203301	0.979772	-0.755686
H	2.036850	0.308412	2.482308
H	3.137830	0.093449	1.104176
H	2.041182	-0.427071	-2.291026
H	3.120881	-0.103863	-0.931822
C	1.360060	-1.366833	-0.412392
P	0.023765	-2.075272	-1.408857
C	-2.083238	-0.228653	-1.224629
C	2.074927	-0.239272	-1.217006
C	-1.174727	-1.036712	0.928685
C	1.278422	-1.099329	0.943286
C	0.023328	-1.253655	1.661816
C	-1.251557	-1.296334	-0.453143

C	-2.081202	0.151461	1.401405
C	2.087986	0.153984	1.403742
C	0.014270	-1.123163	3.077194
H	-3.127338	-0.172226	-0.909661
H	-2.061357	-0.406660	-2.299757
H	-0.891081	1.080973	-3.348694
H	0.839875	1.047893	-3.354960
N	0.011700	-1.060332	4.241891

16

E_{tot} = –8.519

N_{imag} = 0

H	0.746666	-3.196339	2.438991
C	-0.436283	-3.320103	0.673628
C	0.776189	-3.277047	1.353803
H	2.077767	-1.321677	2.435568
H	-1.706567	-2.531057	-2.420239
C	2.016246	-2.646953	-0.700504
C	-0.522863	-3.384221	-0.748986
P	0.870609	-3.548970	-1.801825
C	1.885504	-2.629852	0.673933
H	2.188022	-1.239633	-2.412997
H	3.169739	-0.765177	-1.010752
H	3.135425	-0.839569	1.092821
C	-0.412878	-0.051236	2.803926
C	0.958555	-0.479059	0.714779
C	-0.278274	-0.434982	1.397983
C	-1.623509	-2.544697	1.342675
C	2.158548	-1.254950	1.352652
C	-1.331359	-1.195120	-0.699866
C	0.971652	-0.524445	-0.711441
C	-0.227131	-0.590190	-1.409145
C	-1.342787	-1.158818	0.689791
C	-1.723893	-2.557862	-1.328527
C	2.229054	-1.229907	-1.320393
H	1.581126	0.773519	2.992523
H	-2.511506	-0.559092	2.942951
H	-1.520419	-2.535123	2.425529
H	-2.601398	-2.955979	1.082012
H	-2.700427	-2.920166	-0.996729
H	-0.202885	-0.681073	-2.493158
C	-0.704968	0.753248	5.509275
C	0.650240	0.564178	3.509028
C	-1.649713	-0.178415	3.481640
C	0.511085	0.944287	4.841394
C	-1.788786	0.204554	4.813624
H	-2.751023	0.091142	5.307696
H	-0.815708	1.059006	6.546704
H	1.346792	1.412070	5.356817

17

E_{tot} = –10.946

N_{imag} = 0

H	0.758917	-3.256902	2.437466
C	-0.423658	-3.346901	0.669066
C	0.786037	-3.318768	1.351043
H	2.080082	-1.365605	2.437534
H	-1.695070	-2.552821	-2.412100
C	2.021675	-2.672855	-0.700460
C	-0.510503	-3.383870	-0.754879
P	0.872711	-3.559128	-1.815501
C	1.897148	-2.672511	0.676185
H	2.203555	-1.281081	-2.398652
H	3.160031	-0.782129	-0.991268
H	3.131599	-0.872483	1.092428
C	-1.779665	0.196526	-4.805695
C	0.947159	-0.547186	0.719934
C	-0.277798	-0.481953	1.419769
C	-1.615068	-2.590793	1.340489
C	2.161402	-1.302732	1.354139
C	-1.348346	-1.198289	-0.685217
C	0.956753	-0.555904	-0.702983
C	-0.268652	-0.490791	-1.407724
C	-1.341774	-1.199538	0.701047
C	-1.712460	-2.569420	-1.324381
C	2.228895	-1.260026	-1.310485
C	-0.689300	0.730838	-5.502743
H	-2.508333	-0.568176	-2.939442
H	-1.515821	-2.584854	2.424047
H	-2.590572	-3.004830	1.073631
H	-2.686558	-2.938008	-0.990945
C	0.533206	0.895944	-4.838755
C	-0.695997	0.739796	5.517667
C	0.671923	0.506431	-3.510188
C	-1.642053	-0.198201	-3.477843
C	0.518695	0.925917	4.845328
C	-1.780472	0.183234	4.828803
H	1.607798	0.699998	-2.997419
C	-0.400130	-0.093724	-2.800867
H	1.586321	0.740243	2.996212
C	0.655845	0.535972	3.515832
C	-1.644647	-0.210401	3.499797

H	-2.745264	0.101295	-5.297078
C	-0.409803	-0.083775	2.816179
H	-2.506423	-0.600573	2.967514
H	-2.740821	0.070503	5.326866
H	-0.798322	1.042879	-6.538442
H	1.375043	1.350892	-5.355724
H	-0.804488	1.053038	6.553065
H	1.355564	1.397218	5.355809

18

E_{tot} = –16.427

N_{imag} = 0

H	0.758443	-3.257534	2.436906
C	-0.424823	-3.356018	0.668804
C	0.786760	-3.323043	1.350647
H	2.077592	-1.369226	2.436777
H	-1.690377	-2.556675	-2.411815
C	2.018698	-2.675844	-0.701348
C	-0.512128	-3.393791	-0.753165
P	0.873201	-3.560676	-1.815555
C	1.894571	-2.676814	0.675920
H	2.204711	-1.282910	-2.397651
H	3.166627	-0.790764	-0.991469
H	3.136660	-0.883038	1.095191
H	0.488677	2.778671	10.267583
C	0.957447	-0.538158	0.716642
C	-0.273515	-0.479246	1.419009
C	-1.610997	-2.593227	1.340800
C	2.162232	-1.306524	1.353433
C	-1.339040	-1.202784	-0.685845
C	0.967539	-0.546630	-0.700045
C	-0.264052	-0.489460	-1.408061
C	-1.332566	-1.203166	0.700816
C	-1.708698	-2.573119	-1.324027
C	2.231333	-1.261959	-1.309356
H	0.492121	2.757839	-10.257129
H	-2.501931	-0.565957	-2.923112
H	-1.510697	-2.586207	2.424339
H	-2.588854	-3.003029	1.075313
H	-2.685013	-2.936774	-0.991174
C	-0.583055	1.256297	6.865045
C	-0.712119	0.744899	5.500342
C	0.728915	1.766745	7.036736
C	-1.502602	1.298858	7.921327
C	0.519006	0.933170	4.820795
C	-1.801672	0.187811	4.816822
C	1.519464	1.605163	5.748629
C	1.119756	2.313355	8.254659
C	-1.102832	1.850202	9.142566
C	0.668800	0.550524	3.500758
C	-1.646005	-0.201912	3.491045
C	0.196024	2.353523	9.310527
C	-0.405399	-0.073973	2.806964
H	-2.510618	0.909620	7.797660
H	-2.767007	0.076700	5.305504
H	1.855525	2.573480	5.351340
H	2.420525	0.992994	5.894780
H	2.125308	2.706433	8.392331