Supplementary Material (ESI) for *PCCP*
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Supplementary information

On the primary event of phytochrome: quantum chemical comparison of photoreactions at C_4, C_{10} and C_{15}

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1. Population analysis

Table S1 Difference in S_1 and S_0 charges (Δq, elementary charge units) of the pyrrole rings along the $Z \rightarrow E$ isomerization paths of *ZaZsZa* PΦB[a]

***ZaZsZa* PΦB**	Dihedral = –45°	Minimum	Dihedral = 45°
$Z \rightarrow E$ isomerization at C4			
Δq(ring A	–0.01 (–0.01)	–0.02 (–0.02)	–0.00 (–0.01)
Δq(ring B)	0.03 (0.04)	0.03 (0.04)	0.04 (0.04)
Δq(ring C)	0.01 (–0.00)	0.02 (0.01)	–0.01 (–0.00)
Δq(ring D)	–0.03 (–0.03)	–0.03 (–0.03)	–0.03 (–0.03)
$Z \rightarrow E$ isomerization at C10			
Δq(ring A)	0.02 (0.02)	–0.02 (–0.02)	0.04 (0.03)
Δq(ring B)	0.09 (0.09)	0.03 (0.04)	0.10 (0.12)
Δq(ring C)	–0.04 (–0.04)	0.02 (0.01)	–0.04 (–0.07)
Δq(ring D)	–0.07 (–0.07)	–0.03 (–0.03)	–0.10 (–0.08)
$Z \rightarrow E$ isomerization at C15			
Δq(ring A)	–0.02 (–0.02)	–0.02 (–0.02)	–0.02 (–0.02)
Δq(ring B)	0.04 (0.02)	0.03 (0.04)	0.03 (0.02)
Δq(ring C)	–0.04 (0.00)	0.02 (0.01)	–0.03 (0.00)
Δq(ring D)	0.02 (0.00)	–0.03 (–0.03)	0.02 (0.00)

[a] Atomic charges derived from standard Mulliken population analysis using HF/SVP and HF/6-311G(2df,p) for the ground state (on B3LYP/SVP geometries) and CIS/SVP and CIS/6-311G(2df,p) for the excited state (on TD-B3LYP/SVP geometries), with Δq values obtained with the 6-311G(2df,p) basis set given in parentheses.

$$q(\text{ring A}) = q(\text{C1}) + q(\text{C2}) + q(\text{C3}) + q(\text{C4}) + q(\text{NA}) + q(\text{O1}) + q(\text{C5}) / 2$$

$$q(\text{ring B}) = q(\text{C5}) / 2 + q(\text{C6}) + q(\text{C7}) + q(\text{C8}) + q(\text{C9}) + q(\text{NB}) + q(\text{C10}) / 2$$

$$q(\text{ring C}) = q(\text{C10}) / 2 + q(\text{C11}) + q(\text{C12}) + q(\text{C13}) + q(\text{C14}) + q(\text{NC}) + q(\text{C15}) / 2$$

$$q(\text{ring D}) = q(\text{C15}) / 2 + q(\text{C16}) + q(\text{C17}) + q(\text{C18}) + q(\text{C19}) + q(\text{ND}) + q(\text{O19}) + q(\text{C18}^1) + q(\text{C18}^2)$$

Table S2 Δq of the pyrrole rings and vertical $S_0 \rightarrow S_1$ excitation energies (ΔE, eV) of *Zs* PΦB-BC at different rotations about the methine bridge[a]

***Zs* PΦB-BC**	C10–C11					
	0°	10°	20°	30°	40°	50°
Δq(ring B) = –Δq(ring C)						
HF/CIS	–0.01	–0.00	0.01	0.03	0.05	0.09
CASSCF(12,11)	–0.02	–0.00	0.02	0.06	0.10	0.16
SA-CASSCF(12,11)[b]	–0.02	–0.00	0.03	0.06	0.11	0.18
ΔE[c]						
CIS	3.83	3.80	3.77	3.72	3.65	3.56
TD-B3LYP	3.46	3.44	3.42	3.38	3.31	3.19
CASSCF(12,11)	3.13	3.11	3.09	3.05	2.98	2.88
SA-CASSCF(12,11)[b]	3.16	3.15	3.12	3.09	3.02	2.93

[a] Atomic charges derived from standard Mulliken population analysis using HF(S_0)/CIS(S_1) and CASSCF (S_0 and S_1) in combination with the SVP basis set and based on B3LYP/SVP ground-state geometries. The (12,11) active space in the CASSCF calculations includes the full π space of PΦB-BC (10 electrons in 10 orbitals) as well as the nitrogen lone pair and the corresponding nonbonding orbital.

$$q(\text{ring B}) = q(\text{C6}) + q(\text{C7}) + q(\text{C8}) + q(\text{C9}) + q(\text{NB}) + q(\text{C10}) / 2$$

$$q(\text{ring C}) = q(\text{C10}) / 2 + q(\text{C11}) + q(\text{C12}) + q(\text{C13}) + q(\text{C14}) + q(\text{NC})$$

[b] Two-root (S_0 and S_1) state-average (with equal weights) calculations for the excited state.
[c] All calculations carried out with the SVP basis set and based on B3LYP/SVP ground-state geometries.

2. Molecular structures

B3LYP/SVP S_0 structure of *ZaZsZa* PΦB

N	5.331373	0.419788	0.021789
C	4.311182	-0.503665	0.005642
C	4.937211	-1.817352	-0.054363
C	6.294675	-1.685705	-0.077370
C	6.591019	-0.203641	-0.057351
C	2.953830	-0.274556	0.041707
C	2.281881	0.973484	0.187737
C	2.741230	2.271251	0.554689
C	1.663364	3.141037	0.499112
C	0.507328	2.401653	0.130787
N	0.927939	1.081202	-0.022742
C	-0.796450	2.885425	-0.024871
C	-2.000453	2.193331	-0.163133
C	-3.265023	2.725484	-0.536567
C	-4.184685	1.690114	-0.570527
C	-3.517132	0.490170	-0.183681
N	-2.201124	0.822452	0.016158
C	-3.971803	-0.851513	-0.005658
C	-5.265732	-1.304371	0.052553
N	-6.412887	-0.569528	0.023466
C	-7.608493	-1.321598	0.087078
C	-7.191820	-2.785787	0.113281
C	-5.655476	-2.768208	0.186761
O	-8.702469	-0.833196	0.108406
C	7.291224	-2.735126	-0.117413
C	8.624054	-2.538318	-0.137714
O	7.641856	0.385153	-0.105750
H	-5.219175	1.774888	-0.892874
H	-3.443520	3.767519	-0.797198
H	3.747278	2.523837	0.878721
H	1.666268	4.202520	0.741664
H	4.370097	-2.747725	-0.056425
H	0.398540	0.372958	-0.518289
H	-1.559710	0.217633	0.516285
H	-0.885663	3.974389	-0.038943
H	2.326107	-1.163532	-0.057594
H	5.237544	1.422609	-0.077822
H	6.896137	-3.756759	-0.131402
H	9.307990	-3.389896	-0.168636
H	9.053514	-1.534748	-0.125521
H	-3.199795	-1.617302	0.106308
H	-5.280056	-3.157943	1.146939
H	-5.176911	-3.364076	-0.604850
H	-6.457531	0.444286	0.034412
H	-7.576360	-3.271869	-0.797088
H	-7.676555	-3.282494	0.966207

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TD-B3LYP/SVP S_1 structure of *ZaZsZa* PΦB

C	-5.430699	-2.798924	0.315735
C	-5.120480	-1.324578	0.118824
N	-6.304025	-0.656916	0.024208
C	-7.458200	-1.471468	0.087483
C	-6.961288	-2.907351	0.195150
C	-3.847433	-0.795844	0.069820
C	-3.452975	0.546815	-0.172876
C	-4.168067	1.700933	-0.628220
C	-3.297531	2.772167	-0.662744
C	-1.999319	2.314680	-0.249612
N	-2.143616	0.946535	0.004062
C	-0.829225	3.045130	-0.127706
C	0.487390	2.532199	0.133188
C	1.606166	3.197210	0.667338
C	2.679204	2.286445	0.694671
C	2.227122	1.063145	0.169987
N	0.878983	1.230375	-0.127056
C	2.866706	-0.201753	-0.046027
C	4.216401	-0.484040	-0.048013
N	5.275564	0.396046	0.090538
C	6.509251	-0.262434	0.025639
C	6.162061	-1.722058	-0.136295
C	4.787231	-1.804845	-0.188078
C	7.105577	-2.803841	-0.229745
C	8.457065	-2.663716	-0.180065
O	7.591990	0.274189	0.082940
O	-8.578469	-1.045334	0.052363
H	-5.205773	1.723477	-0.953500
H	-3.517419	3.788246	-0.986542
H	3.663617	2.478895	1.115532
H	1.611868	4.225422	1.023760
H	4.191819	-2.711632	-0.298316
H	0.370303	0.613064	-0.751611
H	-1.477340	0.414286	0.553584
H	-0.916907	4.129272	-0.221681
H	2.212521	-1.057074	-0.239098
H	5.214408	1.407076	0.092588
H	6.675546	-3.804701	-0.350448
H	9.106659	-3.539329	-0.258284
H	8.919333	-1.680697	-0.063143
H	-3.040739	-1.513074	0.248697
H	-5.067716	-3.120351	1.306869
H	-4.892931	-3.407966	-0.427542
H	-6.404050	0.352836	-0.016835
H	-7.286912	-3.454923	-0.703934
H	-7.446540	-3.393184	1.054520

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TD-B3LYP/SVP S_2 structure of *ZaZsZa* PΦB

C	-5.544404	-2.802230	0.223763
C	-5.179294	-1.334953	0.065766
N	-6.340183	-0.615579	0.030907
C	-7.520840	-1.382753	0.110243
C	-7.081934	-2.841581	0.152527
C	-3.897829	-0.844642	-0.009089
C	-3.484733	0.510055	-0.218205
C	-4.166895	1.666503	-0.670693
C	-3.272092	2.736856	-0.653562
C	-2.011927	2.256536	-0.211096
N	-2.174176	0.892619	0.012865
C	-0.817531	2.980965	-0.025920
C	0.480326	2.482062	0.164238
C	1.644431	3.193942	0.571492
C	2.710148	2.302080	0.613090
C	2.238873	1.024734	0.212447
N	0.877521	1.159035	-0.011559
C	2.890867	-0.232854	0.047981
C	4.240153	-0.499011	0.004645
N	5.303159	0.386304	0.029960
C	6.558315	-0.249859	-0.037651
C	6.236062	-1.699586	-0.092256
C	4.851318	-1.819790	-0.068571
C	7.193169	-2.766310	-0.168913
C	8.550928	-2.590283	-0.193111
O	7.627459	0.323446	-0.054742
O	-8.625092	-0.913479	0.130971
H	-5.189908	1.705624	-1.038465
H	-3.469324	3.760329	-0.967570
H	3.715332	2.533466	0.958972
H	1.660026	4.247026	0.846715
H	4.281251	-2.749512	-0.090771
H	0.345859	0.493275	-0.561328
H	-1.541750	0.345759	0.587138
H	-0.914072	4.068316	-0.035522
H	2.244009	-1.108477	-0.059741
H	5.232147	1.398219	-0.003436
H	6.786711	-3.782864	-0.213034
H	9.218448	-3.453706	-0.244097
H	8.985354	-1.588065	-0.163948
H	-3.102217	-1.584500	0.118915
H	-5.164172	-3.174051	1.190006
H	-5.060275	-3.406224	-0.558978
H	-6.393732	0.398834	0.028080
H	-7.460584	-3.343307	-0.752343
H	-7.558954	-3.335817	1.011616

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B3LYP/TZVP S_0 structure of *ZaZsZa* PΦB

N	5.319574	0.430849	0.037333
C	4.307110	-0.501272	0.023059
C	4.943726	-1.804030	-0.034418
C	6.292061	-1.665750	-0.075335
C	6.580679	-0.186009	-0.071748
C	2.957048	-0.284473	0.066028
C	2.281340	0.954758	0.211328
C	2.724490	2.246043	0.589572
C	1.648064	3.107314	0.525984
C	0.503762	2.372988	0.141136
N	0.927659	1.052500	-0.007909
C	-0.791554	2.853697	-0.025467
C	-1.988176	2.167423	-0.175177
C	-3.240122	2.697813	-0.564447
C	-4.160627	1.671959	-0.607603
C	-3.511103	0.474584	-0.210836
N	-2.193535	0.795637	-0.001866
C	-3.972586	-0.858694	-0.034964
C	-5.261800	-1.295655	0.036566
N	-6.400969	-0.549793	0.026506
C	-7.600636	-1.289489	0.107964
C	-7.201974	-2.755176	0.118518
C	-5.664919	-2.754125	0.168248
O	-8.688756	-0.789720	0.151472
C	7.286183	-2.710528	-0.116804
C	8.611403	-2.519605	-0.145612
O	7.624805	0.408738	-0.151647
H	-5.178293	1.760827	-0.947562
H	-3.410049	3.729175	-0.830923
H	3.714009	2.499485	0.929243
H	1.645424	4.156821	0.775146
H	4.388909	-2.730207	-0.022174
H	0.421796	0.361571	-0.540069
H	-1.579586	0.204294	0.536356
H	-0.879223	3.933533	-0.038948
H	2.339086	-1.169661	-0.027828
H	5.216197	1.421257	-0.110553
H	6.893727	-3.722915	-0.123344
H	9.284281	-3.366529	-0.176256
H	9.048133	-1.530550	-0.140980
H	-3.212010	-1.624834	0.061759
H	-5.287835	-3.150419	1.113152
H	-5.215120	-3.344532	-0.630135
H	-6.434657	0.458557	0.051925
H	-7.597107	-3.226293	-0.782613
H	-7.669387	-3.246726	0.970784

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TD-B3LYP/TZVP S_1 structure of *ZaZsZa* PΦB

C	4.797959	-1.784606	-0.212774
C	4.217738	-0.477634	-0.052824
N	5.268379	0.405051	0.126038
C	6.504934	-0.246189	0.050463
C	6.164735	-1.698894	-0.146156
C	2.874963	-0.203637	-0.066300
C	2.228988	1.047601	0.165743
C	2.655194	2.252569	0.728693
C	1.577733	3.151845	0.708828
C	0.481031	2.500848	0.138621
N	0.881081	1.207542	-0.144657
C	-0.827826	3.014172	-0.143189
C	-1.987766	2.289979	-0.274145
C	-3.278088	2.744249	-0.697797
C	-4.149065	1.683647	-0.660453
C	-3.449539	0.532366	-0.193044
N	-2.135704	0.920562	-0.019179
C	-3.848829	-0.800868	0.051602
C	-5.117869	-1.315870	0.114098
C	-5.438702	-2.785787	0.312217
C	-6.971772	-2.879907	0.213490
C	-7.453739	-1.442290	0.114227
N	-6.295375	-0.638452	0.034715
O	-8.570315	-1.005512	0.095497
O	7.583701	0.294572	0.124446
C	7.104147	-2.775236	-0.252990
C	8.448048	-2.645933	-0.185972
H	-5.172923	1.709128	-0.995447
H	-3.490023	3.747504	-1.032540
H	3.618063	2.441318	1.173870
H	1.571472	4.159862	1.090845
H	4.214080	-2.683777	-0.346406
H	0.402700	0.622348	-0.813659
H	-1.493617	0.406112	0.565178
H	-0.908736	4.088117	-0.248990
H	2.232584	-1.049847	-0.285560
H	5.203886	1.410232	0.122991
H	6.676078	-3.762682	-0.400479
H	9.085197	-3.516182	-0.277643
H	8.918739	-1.682503	-0.041983
H	-3.051447	-1.517125	0.219748
H	-5.073122	-3.110535	1.289762
H	-4.928119	-3.392556	-0.437010
H	-6.386957	0.366827	0.004791
H	-7.307668	-3.418563	-0.674440
H	-7.439596	-3.355631	1.074990

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B3LYP/SVP S_0 structure of *ZsZsZa* PΦB

C	4.343829	3.446571	0.369546
C	4.030870	1.993024	0.061991
N	2.681271	1.915812	-0.204341
C	1.962859	3.105516	-0.025551
C	2.966412	4.135350	0.476678
C	4.903209	0.941393	0.039898
C	4.560257	-0.438892	-0.143368
C	5.408252	-1.527490	-0.462395
C	4.643684	-2.689529	-0.451464
C	3.304618	-2.342218	-0.139973
N	3.285397	-0.947284	0.008520
C	2.187582	-3.173789	-0.000838
C	0.845343	-2.804603	0.126031
C	-0.262250	-3.605118	0.522857
C	-1.393582	-2.805272	0.555687
C	-1.021138	-1.489688	0.145830
N	0.335092	-1.520336	-0.068343
C	-1.751683	-0.281294	-0.030506
C	-3.119086	-0.109117	-0.039052
N	-4.101592	-1.067363	0.040549
C	-5.385853	-0.492028	-0.027369
C	-5.144001	0.998038	-0.115744
C	-3.792015	1.178644	-0.133834
C	-6.178009	2.009280	-0.171660
C	-7.503294	1.765495	-0.153777
O	-6.414560	-1.119676	-0.020914
O	0.780397	3.206594	-0.232011
H	6.469402	-1.442159	-0.687343
H	4.984489	-3.698536	-0.678608
H	-2.379993	-3.114205	0.891601
H	-0.197004	-4.655015	0.804237
H	-3.255457	2.125418	-0.189691
H	0.805185	-0.812676	-0.618630
H	2.609325	-0.496474	0.618043
H	2.391542	-4.246781	0.024806
H	-1.165814	0.631437	-0.173038
H	-3.974086	-2.069988	-0.012661
H	-5.819657	3.042525	-0.233466
H	-8.217483	2.591069	-0.200968
H	-7.896943	0.749009	-0.094177
H	5.964297	1.162809	0.166396
H	4.945250	3.868560	-0.453079
H	4.949902	3.535629	1.282466
H	2.247690	1.125932	-0.668054
H	2.701074	4.402249	1.512497
H	2.874381	5.054398	-0.119561

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TD-B3LYP/SVP S_1 structure of *ZsZsZa* PΦB

N	2.289936	1.894014	-0.086507
C	3.615312	2.180852	0.130747
C	3.712799	3.667699	0.416326
C	2.248890	4.162187	0.470918
C	1.405040	2.964868	0.053890
C	4.646385	1.267006	0.062391
C	4.509050	-0.133043	-0.126479
C	5.497967	-1.097255	-0.495386
C	4.900723	-2.340406	-0.560142
C	3.506448	-2.193712	-0.228707
N	3.306892	-0.814746	-0.005156
C	2.502460	-3.132810	-0.130625
C	1.109923	-2.822473	0.119656
C	0.111137	-3.564051	0.761398
C	-1.072319	-2.785245	0.768543
C	-0.798052	-1.574118	0.122228
N	0.542829	-1.607901	-0.235991
C	-1.567932	-0.378025	-0.122504
C	-2.933300	-0.234942	-0.106536
C	-3.628398	1.026937	-0.258524
C	-4.987134	0.813569	-0.185597
C	-5.192918	-0.671213	0.005564
N	-3.903193	-1.209204	0.061128
O	-6.220798	-1.303322	0.089098
C	-6.029392	1.799859	-0.281124
C	-7.361228	1.533275	-0.209603
O	0.213319	2.873012	-0.128502
H	6.537807	-0.859035	-0.714883
H	5.370659	-3.280636	-0.844895
H	-2.004409	-3.051998	1.262645
H	0.247138	-4.544901	1.213122
H	-3.114126	1.980365	-0.387511
H	0.922761	-1.032887	-0.980782
H	2.606925	-0.528228	0.674833
H	2.780023	-4.186266	-0.202440
H	-1.007800	0.542519	-0.321409
H	-3.743860	-2.209551	0.088572
H	-5.697216	2.834548	-0.422584
H	-8.091830	2.342264	-0.290167
H	-7.725757	0.512678	-0.072401
H	5.664203	1.655399	0.136960
H	4.285260	4.162240	-0.387094
H	4.265959	3.851244	1.350464
H	1.961655	1.002217	-0.438975
H	1.937090	4.476569	1.480203
H	2.037342	5.007048	-0.201359

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TD-B3LYP/SVP S_2 structure of *ZsZsZa* PΦB

C	-3.657730	1.077305	-0.158747
C	-2.945365	-0.203613	-0.042225
N	-3.945456	-1.155818	0.015739
C	-5.243406	-0.606320	-0.048299
C	-5.021344	0.860626	-0.154392
C	-1.590400	-0.368976	-0.002744
C	-0.836983	-1.577516	0.186305
C	-1.154352	-2.866558	0.666045
C	0.010939	-3.644078	0.641917
C	1.071490	-2.835390	0.164645
N	0.521257	-1.580857	-0.076584
C	2.441852	-3.142832	-0.022043
C	3.475826	-2.210923	-0.195257
C	4.836979	-2.407597	-0.556580
C	5.478461	-1.167286	-0.541388
C	4.536241	-0.180769	-0.175502
N	3.313056	-0.829067	-0.008977
C	4.711412	1.229087	0.003779
C	3.713027	2.168107	0.058831
C	3.830639	3.650732	0.361850
C	2.371628	4.135496	0.527705
C	1.507084	2.972500	0.054702
N	2.375918	1.909554	-0.171061
O	0.307857	2.904913	-0.095446
O	-6.267296	-1.253134	-0.025779
C	-6.058199	1.854934	-0.252270
C	-7.396834	1.581740	-0.245851
H	6.518183	-0.968296	-0.796463
H	5.275077	-3.367357	-0.825063
H	-2.117417	-3.186264	1.059782
H	0.115334	-4.673553	0.979864
H	-3.144483	2.038200	-0.226143
H	0.950416	-0.922677	-0.716329
H	2.643209	-0.498878	0.681351
H	2.718580	-4.198352	-0.011398
H	-1.012275	0.553878	-0.125614
H	-3.804813	-2.161866	0.034426
H	-5.724942	2.894886	-0.338639
H	-8.125263	2.392682	-0.320449
H	-7.759690	0.554319	-0.167989
H	5.739972	1.584166	0.096851
H	4.330067	4.159373	-0.480984
H	4.452525	3.829089	1.251360
H	2.043523	1.045504	-0.583015
H	2.111038	4.356266	1.576144
H	2.127245	5.035945	-0.054598

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B3LYP/TZVP S_0 structure of *ZsZsZa* PΦB

C	4.953076	3.124516	0.360621
C	4.378070	1.753419	0.061173
N	3.035132	1.915734	-0.183244
C	2.557719	3.227333	-0.040739
C	3.731487	4.060904	0.444103
C	5.063994	0.582429	0.024076
C	4.534014	-0.727489	-0.166375
C	5.239069	-1.899221	-0.504701
C	4.352145	-2.959170	-0.486506
C	3.071655	-2.470581	-0.151539
N	3.207573	-1.079155	-0.003131
C	1.896906	-3.198032	-0.002015
C	0.586706	-2.759603	0.148810
C	-0.540225	-3.524364	0.532880
C	-1.640249	-2.694783	0.585114
C	-1.232572	-1.391267	0.200989
N	0.123823	-1.453176	-0.009916
C	-1.935535	-0.170573	0.045153
C	-3.290966	0.018650	0.007863
N	-4.285634	-0.930595	0.040901
C	-5.558470	-0.336445	-0.069621
C	-5.294891	1.148067	-0.096295
C	-3.948850	1.309863	-0.064027
C	-6.306257	2.175274	-0.148005
C	-7.628318	1.961650	-0.169200
O	-6.591936	-0.950590	-0.134530
O	1.420452	3.548316	-0.264801
H	6.289227	-1.934843	-0.744861
H	4.570458	-3.989161	-0.721717
H	-2.624186	-2.975598	0.919493
H	-0.508970	-4.571641	0.789509
H	-3.407847	2.244275	-0.069391
H	0.610958	-0.753721	-0.546423
H	2.614202	-0.568108	0.635076
H	2.022880	-4.274171	0.005088
H	-1.337807	0.727150	-0.062755
H	-4.166686	-1.921411	-0.091401
H	-5.930524	3.193687	-0.170103
H	-8.315399	2.796700	-0.209100
H	-8.048567	0.965665	-0.149269
H	6.138745	0.639057	0.136777
H	5.626476	3.416678	-0.448359
H	5.541354	3.106503	1.277355
H	2.459174	1.218619	-0.630102
H	3.523561	4.390454	1.463727
H	3.817494	4.954926	-0.171736

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TD-B3LYP/TZVP S_1 structure of *ZsZsZa* PΦB

N	2.555119	1.919508	-0.100456
C	3.905838	2.018939	0.112549
C	4.208898	3.470346	0.420930
C	2.827562	4.151064	0.535591
C	1.829748	3.103093	0.070220
C	4.805611	0.988645	0.018938
C	4.509689	-0.376702	-0.172134
C	5.394808	-1.429053	-0.540667
C	4.688575	-2.603558	-0.593290
C	3.321123	-2.331003	-0.250594
N	3.243880	-0.933982	-0.047437
C	2.264380	-3.188570	-0.124701
C	0.900444	-2.804423	0.150693
C	-0.107814	-3.498362	0.811923
C	-1.264080	-2.690614	0.814670
C	-0.965575	-1.504905	0.149255
N	0.374815	-1.577251	-0.213021
C	-1.709197	-0.306964	-0.114673
C	-3.064451	-0.140975	-0.094906
C	-3.744854	1.116804	-0.275478
C	-5.099418	0.925129	-0.201987
C	-5.326141	-0.547490	0.021847
N	-4.043781	-1.098269	0.111368
O	-6.360667	-1.166850	0.105033
C	-6.118911	1.923746	-0.322899
C	-7.448820	1.691445	-0.247734
O	0.641746	3.187892	-0.121347
H	6.440987	-1.292331	-0.765889
H	5.063683	-3.576354	-0.869517
H	-2.188046	-2.922236	1.318611
H	0.000937	-4.467866	1.270605
H	-3.228334	2.053768	-0.426991
H	0.766092	-1.023890	-0.960230
H	2.590887	-0.582955	0.641050
H	2.469006	-4.248509	-0.199043
H	-1.135996	0.585439	-0.346764
H	-3.899610	-2.095572	0.122607
H	-5.768575	2.938436	-0.487627
H	-8.151879	2.507911	-0.349863
H	-7.842157	0.696716	-0.087069
H	5.854705	1.245803	0.090027
H	4.801073	3.898916	-0.392574
H	4.805109	3.560490	1.329116
H	2.110989	1.106013	-0.500081
H	2.581605	4.431675	1.561853
H	2.726163	5.046617	-0.076196

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PBE0/SVP S_0 structure of *ZaZsZa* PΦB

N	5.294702	0.417076	0.017690
C	4.289708	-0.513196	0.016557
C	4.925370	-1.817710	-0.039929
C	6.276706	-1.669206	-0.075145
C	6.553253	-0.189384	-0.069660
C	2.934998	-0.297007	0.061586
C	2.264548	0.948802	0.207648
C	2.724797	2.236276	0.591029
C	1.653497	3.108042	0.527357
C	0.505699	2.375071	0.139883
N	0.921882	1.061897	-0.018292
C	-0.792192	2.860997	-0.026975
C	-1.990439	2.169044	-0.175409
C	-3.246250	2.698227	-0.565319
C	-4.160624	1.663763	-0.606454
C	-3.495015	0.472338	-0.205220
N	-2.189862	0.806309	0.007663
C	-3.950497	-0.865045	-0.026892
C	-5.245838	-1.302054	0.042304
N	-6.377114	-0.553904	0.031956
C	-7.574759	-1.287477	0.105401
C	-7.178642	-2.748518	0.112681
C	-5.651425	-2.752586	0.172183
O	-8.659250	-0.787792	0.146250
C	7.285114	-2.701819	-0.115132
C	8.610410	-2.478745	-0.146907
O	7.593992	0.407724	-0.133887
H	-5.189714	1.742994	-0.948089
H	-3.421896	3.738677	-0.834430
H	3.726451	2.480494	0.935620
H	1.655134	4.167385	0.779424
H	4.368858	-2.754390	-0.029541
H	0.397293	0.360307	-0.526060
H	-1.554328	0.206242	0.518676
H	-0.880821	3.949977	-0.041452
H	2.312173	-1.189819	-0.030730
H	5.186807	1.416105	-0.093662
H	6.907993	-3.729947	-0.118616
H	9.310967	-3.316422	-0.176919
H	9.017396	-1.465294	-0.145226
H	-3.184311	-1.637303	0.076638
H	-5.271960	-3.149928	1.127093
H	-5.185903	-3.350635	-0.624793
H	-6.405670	0.459153	0.055118
H	-7.579037	-3.217879	-0.799024
H	-7.665137	-3.247683	0.962422

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TD-PBE0/SVP S_1 structure of *ZaZsZa* PΦB

C	4.737546	-1.797422	-0.220920
C	4.176398	-0.482281	-0.064217
N	5.224314	0.387982	0.109084
C	6.452389	-0.272853	0.051193
C	6.105729	-1.721921	-0.144432
C	2.826392	-0.189656	-0.084835
C	2.198763	1.063515	0.144837
C	2.658448	2.279631	0.689631
C	1.601815	3.190613	0.672274
C	0.476996	2.539788	0.126622
N	0.860536	1.246006	-0.149774
C	-0.825344	3.058302	-0.120651
C	-1.994122	2.321200	-0.253367
C	-3.286244	2.769898	-0.663717
C	-4.146725	1.691604	-0.632660
C	-3.421634	0.550841	-0.182049
N	-2.123468	0.961468	-0.005058
C	-3.798371	-0.794350	0.057576
C	-5.064891	-1.328769	0.115331
C	-5.365009	-2.795906	0.307488
C	-6.886033	-2.908623	0.203555
C	-7.388071	-1.483612	0.108181
N	-6.244623	-0.667194	0.036134
O	-8.507241	-1.064581	0.086843
O	7.529027	0.260873	0.135953
C	7.050178	-2.799164	-0.239316
C	8.392998	-2.655223	-0.161759
H	-5.182837	1.705887	-0.963572
H	-3.513811	3.784760	-0.985112
H	3.640887	2.457475	1.121379
H	1.611275	4.212281	1.046511
H	4.139217	-2.697935	-0.358439
H	0.351346	0.645408	-0.788029
H	-1.450283	0.434678	0.539310
H	-0.919176	4.143952	-0.179600
H	2.173200	-1.034453	-0.319945
H	5.166956	1.397545	0.120311
H	6.623460	-3.797392	-0.385622
H	9.047742	-3.526018	-0.244156
H	8.848947	-1.672788	-0.017675
H	-2.985550	-1.506564	0.225088
H	-4.988739	-3.118553	1.292442
H	-4.831201	-3.398811	-0.442527
H	-6.346740	0.341266	0.001741
H	-7.221164	-3.452333	-0.693371
H	-7.362370	-3.400250	1.063598

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PBE0/SVP S_0 structure of *ZsZsZa* PΦB

C	4.265384	3.447012	0.382340
C	3.982427	1.998696	0.065032
N	2.642556	1.898630	-0.209667
C	1.906536	3.068054	-0.024464
C	2.883495	4.103338	0.491841
C	4.870204	0.964599	0.039049
C	4.540611	-0.413951	-0.154033
C	5.393139	-1.488761	-0.489311
C	4.639785	-2.653233	-0.475849
C	3.306580	-2.315806	-0.148275
N	3.279461	-0.930361	0.008641
C	2.198627	-3.151902	-0.000793
C	0.860776	-2.783500	0.134790
C	-0.238214	-3.577317	0.551538
C	-1.364338	-2.776662	0.589342
C	-0.992338	-1.471900	0.160501
N	0.353293	-1.507746	-0.067209
C	-1.721447	-0.266748	-0.020702
C	-3.085767	-0.105755	-0.034678
N	-4.055030	-1.068357	0.038795
C	-5.336773	-0.507967	-0.036846
C	-5.111347	0.978720	-0.120392
C	-3.765351	1.173577	-0.131479
C	-6.154550	1.974733	-0.179115
C	-7.472235	1.707830	-0.167358
O	-6.356889	-1.142120	-0.039736
O	0.727071	3.151706	-0.235456
H	6.450845	-1.392600	-0.725861
H	4.984264	-3.658770	-0.713073
H	-2.346712	-3.077707	0.944732
H	-0.170355	-4.623829	0.845015
H	-3.236621	2.125113	-0.182587
H	0.818380	-0.808364	-0.630266
H	2.606214	-0.487026	0.625716
H	2.406167	-4.224181	0.025300
H	-1.140035	0.648789	-0.163728
H	-3.916846	-2.067950	-0.021785
H	-5.811776	3.013127	-0.237459
H	-8.200599	2.520542	-0.216169
H	-7.845908	0.683134	-0.111336
H	5.927413	1.199413	0.171345
H	4.859159	3.884189	-0.437350
H	4.870734	3.540688	1.294664
H	2.230015	1.105901	-0.685235
H	2.607262	4.350537	1.529199
H	2.773750	5.028824	-0.090330

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TD-PBE0/SVP S_1 structure of *ZsZsZa* PΦB

N	-3.838884	-1.223105	0.062505
C	-2.888916	-0.246333	-0.119187
C	-3.584940	1.006521	-0.267122
C	-4.935787	0.785884	-0.179338
C	-5.127785	-0.694562	0.014328
C	-1.521196	-0.386040	-0.152522
C	-0.755457	-1.569354	0.091898
C	-1.027944	-2.781553	0.740540
C	0.150734	-3.547993	0.745812
C	1.150352	-2.802974	0.107976
N	0.581672	-1.600771	-0.254293
C	2.538443	-3.102752	-0.128673
C	3.526968	-2.146766	-0.219733
C	4.919964	-2.268472	-0.536540
C	5.490836	-1.016523	-0.463131
C	4.480830	-0.079270	-0.104267
N	3.298850	-0.782552	0.002508
C	4.583192	1.318871	0.088119
C	3.527135	2.200504	0.142835
N	2.221878	1.875444	-0.095915
C	1.308742	2.914925	0.031110
C	2.106077	4.127017	0.461638
C	3.574719	3.679830	0.431072
O	0.127254	2.790180	-0.171956
C	-5.988166	1.758697	-0.261234
C	-7.308200	1.473359	-0.173966
O	-6.144008	-1.334943	0.104235
H	6.526991	-0.756230	-0.673367
H	5.410320	-3.198925	-0.817940
H	-1.960649	-3.048845	1.233068
H	0.290979	-4.524925	1.204071
H	-3.075808	1.961433	-0.402010
H	0.964450	-1.031227	-1.000241
H	2.587300	-0.514202	0.676915
H	2.831340	-4.152254	-0.187571
H	-0.969450	0.534898	-0.373024
H	-3.672906	-2.221065	0.075847
H	-5.669611	2.796725	-0.405270
H	-8.051883	2.270594	-0.245709
H	-7.655941	0.447451	-0.032633
H	5.588702	1.733709	0.178013
H	4.146497	4.190945	-0.361429
H	4.108404	3.877001	1.372929
H	1.928936	0.975256	-0.455019
H	1.766056	4.429923	1.464475
H	1.878097	4.966637	-0.210654

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BP86/SVP S_0 structure of *ZsZsZa* PΦB

C	4.432074	3.428502	0.379482
C	4.084491	1.978843	0.073929
N	2.727538	1.925023	-0.173254
C	2.030963	3.143725	-0.012830
C	3.071651	4.161800	0.454326
C	4.943717	0.900448	0.032055
C	4.578904	-0.474029	-0.152443
C	5.416291	-1.578690	-0.484966
C	4.635031	-2.737409	-0.477976
C	3.294112	-2.374647	-0.153270
N	3.286934	-0.973136	0.000125
C	2.166415	-3.201602	0.000091
C	0.820108	-2.817584	0.140256
C	-0.296107	-3.606700	0.563370
C	-1.426633	-2.792282	0.588468
C	-1.046187	-1.479863	0.148965
N	0.321031	-1.526925	-0.071962
C	-1.771356	-0.269149	-0.042244
C	-3.151341	-0.087866	-0.049413
N	-4.136118	-1.052047	0.033638
C	-5.430212	-0.474093	-0.034877
C	-5.186443	1.019896	-0.122256
C	-3.820386	1.201893	-0.143328
C	-6.221204	2.030969	-0.174545
C	-7.557058	1.780413	-0.153821
O	-6.467282	-1.111966	-0.029218
O	0.839017	3.267027	-0.213216
H	6.484577	-1.502927	-0.720249
H	4.964014	-3.756340	-0.717311
H	-2.419265	-3.086323	0.947411
H	-0.234961	-4.658070	0.870675
H	-3.279654	2.156076	-0.198665
H	0.797132	-0.839724	-0.658890
H	2.622837	-0.528126	0.642259
H	2.363688	-4.284324	0.028080
H	-1.179524	0.647888	-0.199591
H	-4.003008	-2.062321	-0.027768
H	-5.863905	3.074100	-0.236499
H	-8.281127	2.608586	-0.199436
H	-7.944294	0.751768	-0.093786
H	6.019050	1.107110	0.137138
H	5.075033	3.830391	-0.433320
H	5.025023	3.503486	1.313073
H	2.267972	1.120996	-0.607329
H	2.809079	4.485710	1.483558
H	3.006792	5.065690	-0.183543

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TD-BP86/SVP S_1 structure of *ZsZsZa* PΦB

N	-3.878703	-1.163256	0.061059
C	-2.932475	-0.160529	-0.083738
C	-3.677038	1.080861	-0.239334
C	-5.036376	0.826733	-0.190825
C	-5.210330	-0.649787	-0.011491
C	-1.555476	-0.319932	-0.088887
C	-0.805377	-1.526839	0.158420
C	-1.095220	-2.751138	0.802782
C	0.076231	-3.548383	0.783959
C	1.094429	-2.812567	0.139623
N	0.539892	-1.581010	-0.203601
C	2.477658	-3.143007	-0.124720
C	3.501988	-2.210012	-0.245650
C	4.888655	-2.377731	-0.603914
C	5.510879	-1.135693	-0.540705
C	4.540223	-0.156821	-0.148838
N	3.320743	-0.826473	-0.011043
C	4.695123	1.244992	0.046159
C	3.662775	2.171563	0.127624
N	2.335160	1.883119	-0.095568
C	1.440183	2.955157	0.060165
C	2.290754	4.152581	0.481166
C	3.757210	3.656661	0.430743
O	0.237074	2.856841	-0.115067
C	-6.120843	1.778819	-0.300597
C	-7.444064	1.464241	-0.250268
O	-6.204608	-1.352533	0.060857
H	6.556302	-0.910418	-0.782439
H	5.341430	-3.328926	-0.906922
H	-2.027962	-3.005262	1.318765
H	0.201349	-4.539846	1.233197
H	-3.190799	2.057369	-0.362966
H	0.930705	-1.002431	-0.951133
H	2.643615	-0.540508	0.704542
H	2.744313	-4.207724	-0.183498
H	-0.979597	0.602833	-0.282796
H	-3.688494	-2.168387	0.103802
H	-5.818196	2.831335	-0.435953
H	-8.207819	2.250982	-0.341065
H	-7.780225	0.425047	-0.120393
H	5.723866	1.626688	0.115677
H	4.342288	4.164287	-0.366000
H	4.309594	3.830945	1.376304
H	2.013358	0.979981	-0.451269
H	1.973419	4.473387	1.494909
H	2.080029	5.004507	-0.195053

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B3LYP/SVP S_0 structure of *ZaEaZs* PΦB

C	-6.657347	0.705953	-0.390454
C	-5.240563	0.736776	-0.076362
N	-4.879427	-0.557475	0.278338
C	-6.009137	-1.406318	0.288186
C	-7.147513	-0.557307	-0.217149
C	-4.413602	1.831628	-0.147581
C	-2.993112	1.856459	-0.011182
C	-2.158690	2.993443	0.187023
C	-0.844009	2.562572	0.231969
C	-0.828865	1.150431	0.048903
N	-2.166386	0.769911	-0.077452
C	0.196708	0.198026	-0.018842
C	1.580334	0.357238	0.076606
C	2.423222	1.486431	0.296398
C	3.736468	1.056844	0.304782
C	3.748654	-0.358766	0.086265
N	2.445455	-0.732400	-0.037681
C	4.805608	-1.316883	0.023349
C	6.156395	-1.090841	-0.048399
C	7.206626	-2.191019	-0.050965
C	8.559271	-1.458876	-0.040493
C	8.216696	0.017541	-0.183392
N	6.806703	0.103688	-0.146494
O	8.939148	0.966712	-0.301372
O	-5.989018	-2.554991	0.656377
C	-8.497444	-1.025259	-0.454041
C	-8.927793	-2.286763	-0.257633
H	4.600841	1.685537	0.501143
H	2.088544	2.508283	0.450802
H	-2.520532	4.013306	0.301150
H	0.027670	3.191267	0.389714
H	-7.206906	1.575057	-0.751314
H	-2.466542	-0.147967	-0.387177
H	2.146611	-1.683673	-0.220110
H	-0.141325	-0.833835	-0.171131
H	-4.890221	2.795893	-0.331760
H	-4.091579	-0.785658	0.875450
H	-9.198474	-0.266926	-0.819338
H	-9.967845	-2.553442	-0.460294
H	-8.259621	-3.068292	0.109149
H	4.506546	-2.368375	0.028149
H	7.077410	-2.813959	-0.950918
H	7.065641	-2.854644	0.815192
H	6.359366	1.007153	-0.259861
H	9.118113	-1.595114	0.898735
H	9.235405	-1.752296	-0.856519

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TD-B3LYP/SVP S_1 structure of *ZaEaZs* PΦB

N	-4.879820	-0.525050	0.327886
C	-5.233490	0.770527	-0.046097
C	-6.638968	0.750253	-0.357535
C	-7.139502	-0.521064	-0.168923
C	-6.007181	-1.369215	0.342351
C	-4.388633	1.859690	-0.161275
C	-2.966407	1.871772	-0.066780
C	-2.097330	2.972741	0.080889
C	-0.784479	2.493746	0.105588
C	-0.830661	1.081565	-0.047264
N	-2.167294	0.739897	-0.125461
C	0.173899	0.076719	-0.149422
C	1.548528	0.236063	0.023659
C	2.353819	1.353374	0.429991
C	3.678414	0.951878	0.441596
C	3.739749	-0.419679	0.043769
N	2.442387	-0.808839	-0.181955
C	4.818420	-1.337577	-0.099431
C	6.170699	-1.074257	-0.101236
N	6.779830	0.143190	-0.052820
C	8.193504	0.105745	-0.056024
C	8.581069	-1.366829	-0.051608
C	7.254371	-2.135948	-0.182466
O	8.885794	1.084869	-0.057133
C	-8.488116	-0.972315	-0.399089
C	-8.935171	-2.235343	-0.184983
O	-5.998849	-2.519583	0.717374
H	4.516182	1.563768	0.767950
H	1.978140	2.327955	0.727480
H	-2.417114	4.008807	0.176831
H	0.114322	3.096488	0.192331
H	-7.187165	1.617171	-0.727404
H	-2.500222	-0.173439	-0.414180
H	2.177142	-1.727415	-0.518501
H	-0.176809	-0.932429	-0.389261
H	-4.863789	2.824545	-0.352580
H	-4.085134	-0.750600	0.917711
H	-9.185011	-0.214583	-0.774935
H	-9.978483	-2.493460	-0.384300
H	-8.270276	-3.016120	0.190925
H	4.548362	-2.389814	-0.228312
H	7.174313	-2.667916	-1.145662
H	7.110894	-2.891599	0.605405
H	6.300468	1.037659	-0.092316
H	9.115180	-1.581487	0.888189
H	9.292511	-1.555280	-0.869127