Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting information for:

Excitation energies of retinal chromophores: Critical role of the structural model

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1 Vertical excitation energies

Table S1: Multi-state (MS) CASPT2 and quasi-degenerate (QD) NEVPT2 vertical excitation energies (eV) of the RPSB models. For comparison, the SA-CASSCF and the single-state (SS) NEVPT2 and CASPT2 values are also listed. For each model, we indicate the CAS(n,n) active space used in the calculations, which includes all n π electrons in the reference configuration and an equal number n of π orbitals. The results are obtained with the use of the ANO-L-VDZP basis set and the DFT/B3LYP ground-state equilibrium geometries.

	A	B	C	D	E
Method	PSB3(0)	PSB3(1)	PSB4(1)	PSB5(1)	11-*cis*
CAS(n,n)	(6,6)	(6,6)	(8,8)	(10,10)	(12,12)
SA-CASSCF	4.56	4.80	3.74	3.10	2.51
SS-CASPT2/0-IPEA	3.74	3.85	2.99	2.50	1.85[a]
MS-CASPT2/0-IPEA	3.75	3.86	3.04	2.58	2.04[a]
SS-CASPT2/S-IPEA	4.05	4.17	3.32	2.82	2.20
MS-CASPT2/S-IPEA	4.06	4.18	3.35	2.87	2.30
SS-NEVPT2/PC	4.10	4.22	3.37	2.87	
QD-NEVPT2/PC	4.12	4.23	3.41	2.93	
SS-NEVPT2/SC	4.17	4.28	3.43	2.92	2.26
QD-NEVPT2/SC	4.18	4.29	3.45	2.96	

[a] Constant imaginary level shift of 0.1 au.

Table S2: Ground-state (kcal/mol) and vertical excitation (eV) energies of the 11-*cis* RPSB (model E) obtained on the DFT equilibrium geometries optimized with the M06-L, M06, M06-2X, and M06-HF functionals. We list the percent of exact exchange of each functional in parenthesis. The bond length alternation (BLA, Å) and the angle of the β-ionone ring (ϕ, $^\circ$) are also listed.

	Geometry			
	M06-L (0%)	M06 (27%)	M06-2X (54%)	M06-HF (100%)
BLA[a]	0.024	0.032	0.051	0.090
ϕ	-29.1	-33.9	-38.0	-54.7
Ground-state energies[b] (kcal/mol)				
CASPT2/S-IPEA	+1.62	+1.08	0.00	+1.15
NEVPT2/SC	+1.01	+0.72	0.00	+0.83
Vertical excitation energies (eV)				
SA-CASSCF	2.44	2.54	2.71	3.12
SS-CASPT2/S-IPEA	2.18	2.23	2.30	2.53
SS-NEVPT2/SC	2.24	2.29	2.33	2.54

[a] Bond length alternation for C−C bonds from C_5 to C_{15} (Å).
[b] The M06-2X geometry is taken as the zero reference energy.
[c] Constant imaginary level shift of 0.1 au.

Table S3: NEVPT2/SC vertical excitation energies (eV) of the 11-cis RPSB (model E) obtained with different thresholds in the construction of the third- and fourth-order density matrices. The CASSCF wave function is truncated so that only configurations with a weight larger than the given threshold are kept. We observe that a threshold of 10^{-10}, as used in the paper, gives converged results. The results are obtained employing the ANO-L-VDZP basis set and the DFT/B3LYP ground-state equilibrium geometry.

Threshold	Excitation energy
10^{-6}	2.66
10^{-7}	2.13
10^{-8}	2.26
10^{-10}	2.26
No truncation	2.26

Table S4: SA-CASSCF and SS-CASPT2/S-IPEA vertical excitation energies (eV) of the 11-cis RPSB (model E) obtained with different basis sets. We show in boldface the results obtained with the default ANO-L-VDZP basis set. The calculations are performed employing the DFT/B3LYP ground-state equilibrium geometry.

Basis set	SA-CASSCF	SS-CASPT2/S-IPEA
cc-pVDZ	2.79	2.35
aug-cc-pVDZ[a]	2.74	2.33
ANO-L-VDZP	**2.71**	**2.30**
aug-ANO-L-VDZP[a,b]	2.73	2.29
ANO-L-[4s3p1]/[3s1p]	2.73	2.29

[a] Diffuse functions only on the heavy atoms;
[b] Diffuse functions taken from the aug-cc-pVDZ basis set;

2 Geometries

Table S5: DFT/M06-L ground-state equilibrium geometry (Å) of the 11-cis RPSB (model E). The optimization is performed in C1 symmetry and with the cc-pVDZ basis set.

N	7.990021	-0.600808	0.307918
C	6.662472	-0.693623	0.242947
C	5.811034	0.381639	0.048099
C	4.407452	0.320364	-0.020942
C	3.726131	1.538516	-0.224721
C	2.365863	1.823143	-0.326885
C	1.235657	0.993234	-0.283837
C	-0.089785	1.428665	-0.365200
C	-1.113391	0.437971	-0.293092
C	-2.458498	0.715183	-0.273629
C	-3.574223	-0.187605	-0.166642
C	-3.540350	-1.483268	-0.626487
C	-4.665805	-2.439238	-0.384057
C	-5.662488	-1.977817	0.656628
C	-6.028996	-0.536755	0.376012
C	-4.828934	0.412449	0.498286
C	-4.521109	0.680379	1.977033
C	-5.224387	1.734720	-0.172513
C	-2.438766	-2.060571	-1.453584
C	-0.471937	2.865434	-0.510898
C	3.675503	-0.972455	0.120959
C	8.897277	-1.708317	0.505341
H	9.582552	-1.810130	-0.346750
H	9.494808	-1.566230	1.415464
H	8.322058	-2.634009	0.605008
H	8.403485	0.321713	0.205813
H	6.278220	-1.710453	0.358091
H	6.270718	1.368931	-0.062295
H	2.961220	-0.924102	0.954920
H	4.330279	-1.830261	0.301286
H	3.092463	-1.189807	-0.785263
H	4.378899	2.411967	-0.306733
H	2.161284	2.889107	-0.462720
H	1.363563	-0.084079	-0.174524
H	0.381517	3.541974	-0.601804
H	-1.060560	3.199401	0.356208
H	-1.107794	3.013856	-1.394308
H	-0.771635	-0.595042	-0.192540
H	-2.726368	1.776257	-0.249347

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H	-4.230499	-3.421458	-0.129860
H	-5.172784	-2.618687	-1.352204
H	-5.224742	-2.072281	1.663840
H	-6.551051	-2.623635	0.649195
H	-6.825066	-0.185632	1.050061
H	-6.441472	-0.465799	-0.645846
H	-4.294107	-0.244339	2.527277
H	-3.652438	1.346907	2.092197
H	-4.534714	2.561140	0.049059
H	-5.376841	1.164372	2.470746
H	-6.211271	2.050414	0.195542
H	-5.298146	1.631934	-1.264943
H	-1.864095	-1.310530	-2.009567
H	-1.730886	-2.636724	-0.834565
H	-2.853071	-2.781410	-2.173774

Table S6: DFT/M06 ground-state equilibrium geometry (Å) of the 11-cis RPSB (model E). The optimization is performed in C1 symmetry and with the cc-pVDZ basis set.

N	7.979818	-0.602160	0.295415
C	6.656381	-0.697901	0.244576
C	5.803007	0.374160	0.044925
C	4.401079	0.311918	-0.010525
C	3.719499	1.527954	-0.229556
C	2.362479	1.809795	-0.327386
C	1.222817	0.991178	-0.247654
C	-0.090005	1.439353	-0.355193
C	-1.128966	0.460086	-0.251945
C	-2.465017	0.741168	-0.281775
C	-3.576190	-0.177905	-0.168356
C	-3.534603	-1.452467	-0.660966
C	-4.654676	-2.423794	-0.442842
C	-5.629960	-2.007826	0.636851
C	-6.013208	-0.561445	0.410271
C	-4.821384	0.396140	0.529913
C	-4.495502	0.648136	2.005599
C	-5.245049	1.722082	-0.112103
C	-2.437738	-2.010240	-1.509909
C	-0.458279	2.870081	-0.574384
C	3.664634	-0.975079	0.155956
C	8.893601	-1.705597	0.503878
H	9.595405	-1.796001	-0.338532
H	9.472340	-1.566446	1.429421
H	8.321758	-2.639152	0.584569
H	8.386920	0.324378	0.182793
H	6.271019	-1.714904	0.374095
H	6.264165	1.361188	-0.081996
H	2.967962	-0.909277	1.006874
H	4.316360	-1.838894	0.330602
H	3.061732	-1.189483	-0.741086
H	4.372913	2.399912	-0.337385
H	2.162801	2.873240	-0.498294
H	1.337324	-0.082433	-0.089545
H	0.400507	3.549091	-0.609342
H	-1.124986	3.222596	0.228968
H	-1.014698	2.982624	-1.518476
H	-0.800695	-0.572630	-0.097783
H	-2.741725	1.801283	-0.322683
H	-4.210366	-3.415492	-0.235590
H	-5.182621	-2.555446	-1.410253

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H	-5.166250	-2.134330	1.631611
H	-6.517284	-2.659458	0.624369
H	-6.796923	-0.234373	1.114983
H	-6.446839	-0.466004	-0.604352
H	-4.250951	-0.283391	2.541737
H	-3.629925	1.323864	2.115272
H	-4.560947	2.555362	0.115755
H	-5.353127	1.120291	2.514345
H	-6.233905	2.015239	0.277544
H	-5.331121	1.630998	-1.207880
H	-1.816084	-1.244522	-1.992765
H	-1.775399	-2.668436	-0.918036
H	-2.873610	-2.653049	-2.293087

Table S7: DFT/M06-2X ground-state equilibrium geometry (Å) of the 11-cis RPSB (model E). The optimization is performed in C1 symmetry and with the cc-pVDZ basis set.

N	7.931036	-0.651835	0.304760
C	6.614299	-0.717995	0.254617
C	5.782301	0.382356	0.053726
C	4.386010	0.335573	-0.002826
C	3.714244	1.568470	-0.220498
C	2.363841	1.851293	-0.325359
C	1.215956	1.022893	-0.251815
C	-0.086232	1.473358	-0.371967
C	-1.138436	0.489626	-0.262308
C	-2.465603	0.775771	-0.317561
C	-3.569586	-0.172805	-0.188930
C	-3.519777	-1.424226	-0.719522
C	-4.620565	-2.430534	-0.497773
C	-5.568233	-2.056891	0.629933
C	-5.981179	-0.603776	0.460251
C	-4.792967	0.363668	0.577546
C	-4.411022	0.559191	2.053476
C	-5.247279	1.716794	0.003239
C	-2.426830	-1.940510	-1.617037
C	-0.467630	2.906819	-0.600539
C	3.624259	-0.945614	0.156616
C	8.820808	-1.782311	0.516540
H	9.516419	-1.879873	-0.327357
H	9.394591	-1.646560	1.443112
H	8.221063	-2.696315	0.594885
H	8.362842	0.262704	0.191447
H	6.206479	-1.722910	0.383968
H	6.260624	1.357195	-0.070816
H	2.934776	-0.863514	1.008899
H	4.262770	-1.818035	0.321881
H	3.019924	-1.131991	-0.742725
H	4.373646	2.432957	-0.320486
H	2.164183	2.911350	-0.495024
H	1.328792	-0.045920	-0.087297
H	0.386192	3.582435	-0.693255
H	-1.091236	3.261618	0.233471
H	-1.071218	2.991024	-1.515349
H	-0.821253	-0.541597	-0.092228
H	-2.752306	1.827547	-0.400448
H	-4.152328	-3.413320	-0.320387
H	-5.177555	-2.540596	-1.446897

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H	-5.067786	-2.199311	1.600882
H	-6.446814	-2.716374	0.623758
H	-6.741853	-0.315077	1.201988
H	-6.442537	-0.481633	-0.535072
H	-4.151408	-0.395203	2.534521
H	-3.540546	1.227468	2.149197
H	-4.562574	2.539944	0.254428
H	-5.248155	1.011224	2.607559
H	-6.227012	1.977563	0.430940
H	-5.357096	1.668910	-1.090814
H	-1.847376	-1.145544	-2.100073
H	-1.733312	-2.589725	-1.056212
H	-2.875457	-2.572503	-2.398689

Table S8: DFT/M06-HF ground-state equilibrium geometry (Å) of the 11-cis RPSB (model E). The optimization is performed in C1 symmetry and with the cc-pVDZ basis set.

N	7.841221	-0.772932	0.239846
C	6.540623	-0.782801	0.301466
C	5.735726	0.336060	-0.011506
C	4.355102	0.330612	0.027092
C	3.702923	1.569256	-0.324800
C	2.371872	1.866093	-0.425882
C	1.190886	1.050706	-0.281024
C	-0.080701	1.534224	-0.386464
C	-1.178044	0.566597	-0.254300
C	-2.483066	0.878369	-0.350350
C	-3.580145	-0.116144	-0.226366
C	-3.618207	-1.218192	-0.999502
C	-4.702352	-2.270956	-0.851582
C	-5.473437	-2.155408	0.463031
C	-5.870454	-0.693827	0.676272
C	-4.645004	0.225931	0.827040
C	-4.027092	0.081305	2.233410
C	-5.126739	1.682044	0.652914
C	-2.648199	-1.519331	-2.126192
C	-0.448767	2.979845	-0.625113
C	3.547122	-0.881490	0.421365
C	8.717521	-1.904152	0.552036
H	9.302306	-2.163566	-0.338487
H	9.386456	-1.624430	1.375213
H	8.093988	-2.754195	0.850225
H	8.291409	0.092686	-0.053133
H	6.098435	-1.729455	0.614699
H	6.245597	1.252833	-0.310304
H	2.842263	-0.592232	1.212088
H	4.160484	-1.709599	0.786049
H	2.975681	-1.223001	-0.453459
H	4.384035	2.394026	-0.534112
H	2.180554	2.907366	-0.684541
H	1.289415	-0.014437	-0.099276
H	0.417425	3.643765	-0.681338
H	-1.094291	3.319483	0.197421
H	-1.017963	3.054946	-1.562214
H	-0.897318	-0.471746	-0.064188
H	-2.779086	1.919826	-0.493246
H	-4.232211	-3.261929	-0.945478
H	-5.392558	-2.167365	-1.706474

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H	-4.842214	-2.501286	1.294199
H	-6.366040	-2.793540	0.432750
H	-6.501919	-0.583126	1.570765
H	-6.457243	-0.358863	-0.194913
H	-3.745222	-0.961634	2.435290
H	-3.123864	0.705098	2.316821
H	-4.355615	2.406769	0.954591
H	-4.753380	0.409779	2.992784
H	-6.005794	1.843515	1.295121
H	-5.416594	1.872658	-0.391572
H	-2.038558	-0.652160	-2.400394
H	-1.988330	-2.353865	-1.839570
H	-3.225823	-1.848238	-3.003505