

Supporting Information for:

How Methylation Modifies the Photophysics of the Native all-*trans* Retinal Protonated Schiff Base: a CASPT2/MD Study in Gas Phase and in Methanol

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Gas phase

R: H	MECI-9	MECI-11	MECI-13
C ₄ — C ₇	1.444	1.477	1.496
C ₇ = C ₈	1.406	1.376	1.358
C ₈ — C ₉	1.385	1.419	1.454
C ₉ = C ₁₀	1.483	1.430	1.397
C ₁₀ — C ₁₁	1.360	1.367	1.405
C ₁₁ = C ₁₂	1.433	1.475	1.434
C ₁₂ — C ₁₃	1.386	1.379	1.369
C ₁₃ = C ₁₄	1.420	1.421	1.472
C ₁₄ — C ₁₅	1.385	1.395	1.451
C ₁₅ = N ₁₆	1.324	1.313	1.273
N ₁₆ — C ₁₇	1.454	1.459	1.482
N ₁₆ — H ₁₈	0.999	1.001	1.010
ϕ	91.366	92.495	92.509

MeOH

R: H	MECI-9	MECI-11	MECI-13
C ₄ — C ₇	1.484	1.490	1.496
C ₇ = C ₈	1.430	1.381	1.346
C ₈ — C ₉	1.382	1.428	1.476
C ₉ = C ₁₀	1.488	1.429	1.347
C ₁₀ — C ₁₁	1.387	1.377	1.486
C ₁₁ = C ₁₂	1.399	1.470	1.344
C ₁₂ — C ₁₃	1.457	1.496	1.489
C ₁₃ = C ₁₄	1.361	1.342	1.458

C ₁₄ — C ₁₅	1.502	1.508	1.488
C ₁₅ = N ₁₆	1.264	1.263	1.284
N ₁₆ — C ₁₇	1.488	1.483	1.481
N ₁₆ — H ₁₈	1.029	1.030	1.026
ϕ	92.82	96.34	108.87

Table S1a: Selected geometrical parameters (distances in Angstroms angles in grades)
for diverse structures of the native RPSB in solution

Gas phase

R: CH₃	MECI-9	MECI-11	MECI-13
C ₄ — C ₇	1.445	1.479	1.497
C ₇ = C ₈	1.406	1.380	1.372
C ₈ — C ₉	1.384	1.419	1.437
C ₉ = C ₁₀	1.492	1.449	1.442
C ₁₀ — C ₁₁	1.366	1.372	1.392
C ₁₁ = C ₁₂	1.432	1.476	1.445
C ₁₂ — C ₁₃	1.387	1.381	1.365
C ₁₃ = C ₁₄	1.421	1.417	1.472
C ₁₄ — C ₁₅	1.384	1.399	1.455
C ₁₅ = N ₁₆	1.326	1.310	1.270
N ₁₆ — C ₁₇	1.453	1.460	1.483
N ₁₆ — H ₁₈	0.999	1.002	1.010
ϕ	90.17	94.11	91.84

MeOH

R: CH₃	MECI-9	MECI-11	MECI-13
C ₄ — C ₇	1.485	1.487	1.506
C ₇ = C ₈	1.414	1.404	1.387
C ₈ — C ₉	1.391	1.397	1.421
C ₉ = C ₁₀	1.486	1.473	1.556
C ₁₀ — C ₁₁	1.411	1.361	1.347
C ₁₁ = C ₁₂	1.378	1.472	1.461
C ₁₂ — C ₁₃	1.469	1.463	1.354
C ₁₃ = C ₁₄	1.352	1.357	1.448
C ₁₄ — C ₁₅	1.479	1.484	1.548
C ₁₅ = N ₁₆	1.264	1.270	1.262
N ₁₆ — C ₁₇	1.483	1.477	1.497
N ₁₆ — H ₁₈	1.027	1.027	1.041
ϕ	91.37	96.68	96.53

Table S1b: Selected geometrical parameters (distances in Angstroms angles in grades)
for diverse structures of the methylated RPSB in solution