Electronic Supplementary Material (ESI) for Photochemical & Photobiological Sciences.

SUPPORTING INFORMATION

TO

Insights into the Stabilization of Photolabile UV-Absorbers in Sunscreens

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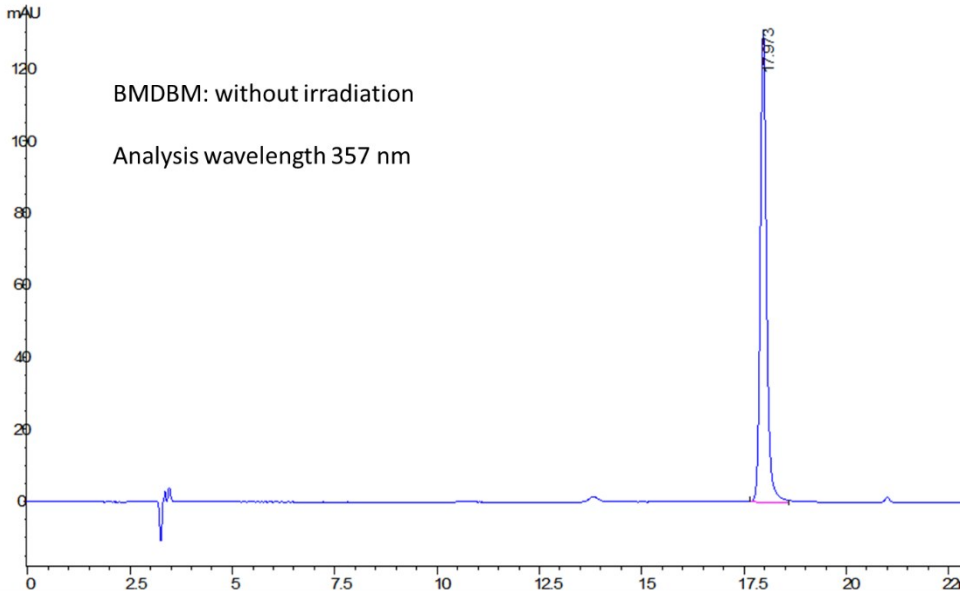
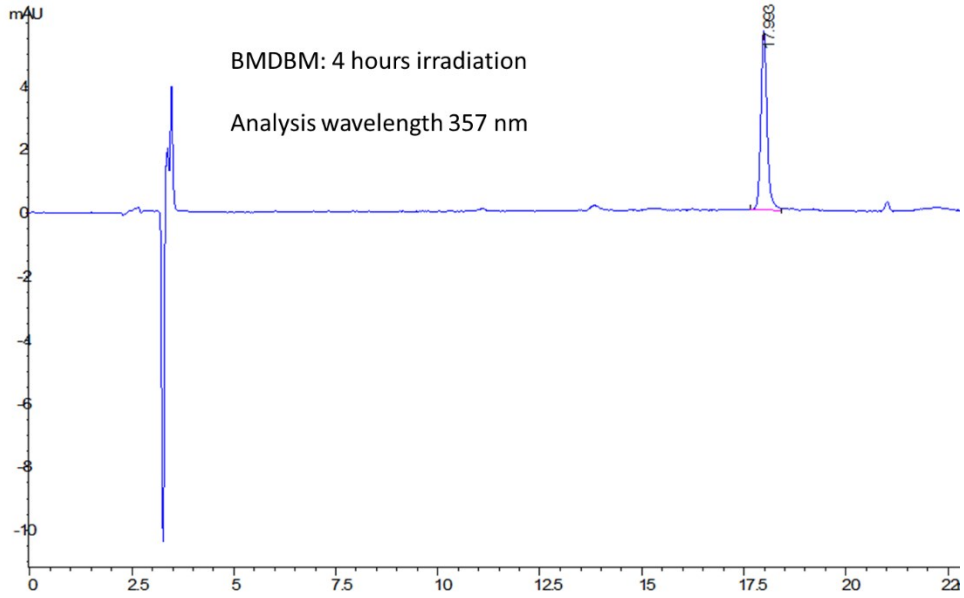
HPLC CHROMATOGRAMS

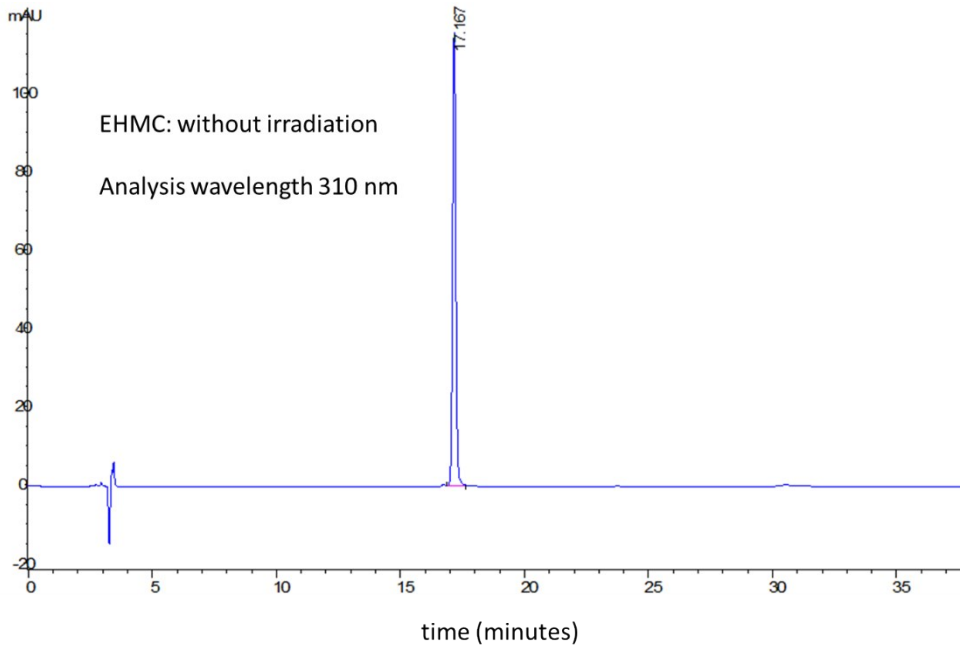
Example HPLC chromatograms are shown in the following for each of the four UV-absorbers when irradiated without any further UV-absorber present at two irradiation conditions, without irradiation and after four hours of irradiation. The application conditions are as described in the experimental section, with BMDBM, EHMC and BEMT at 2% (w/w) in formulation and OCR at 5% (w/w) in formulation, irradiated on quartz plates and rinsed off for analysis.

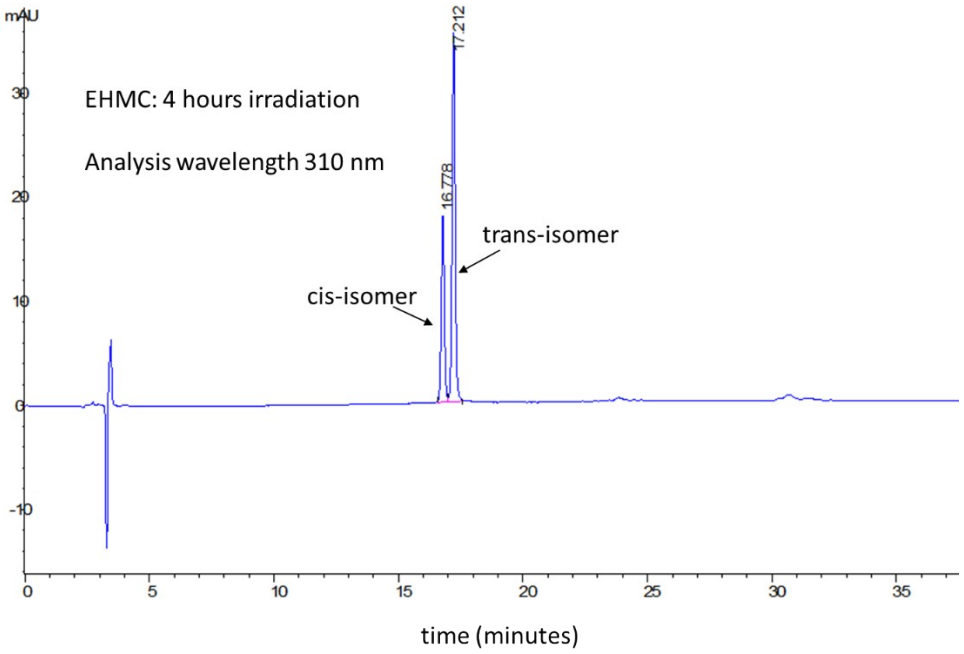
BMDBM


mAU
120
100
80
60
40
20
0
BMDBM: without irradiation
Analysis wavelength 357 nm
17.973
0
2.5
5
7.5
10
12.5
15
17.5
20
22
time (minutes)

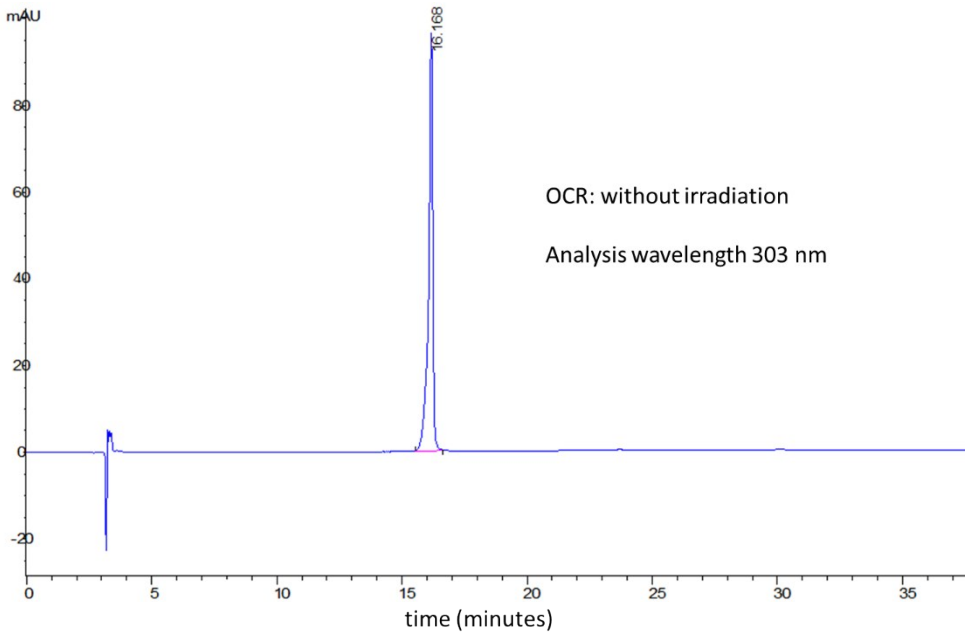

mAU
4
2
0
-2
-4
-6
-8
-10
BMDBM: 4 hours irradiation
Analysis wavelength 357 nm
17.993
0
2.5
5
7.5
10
12.5
15
17.5
20
22
time (minutes)

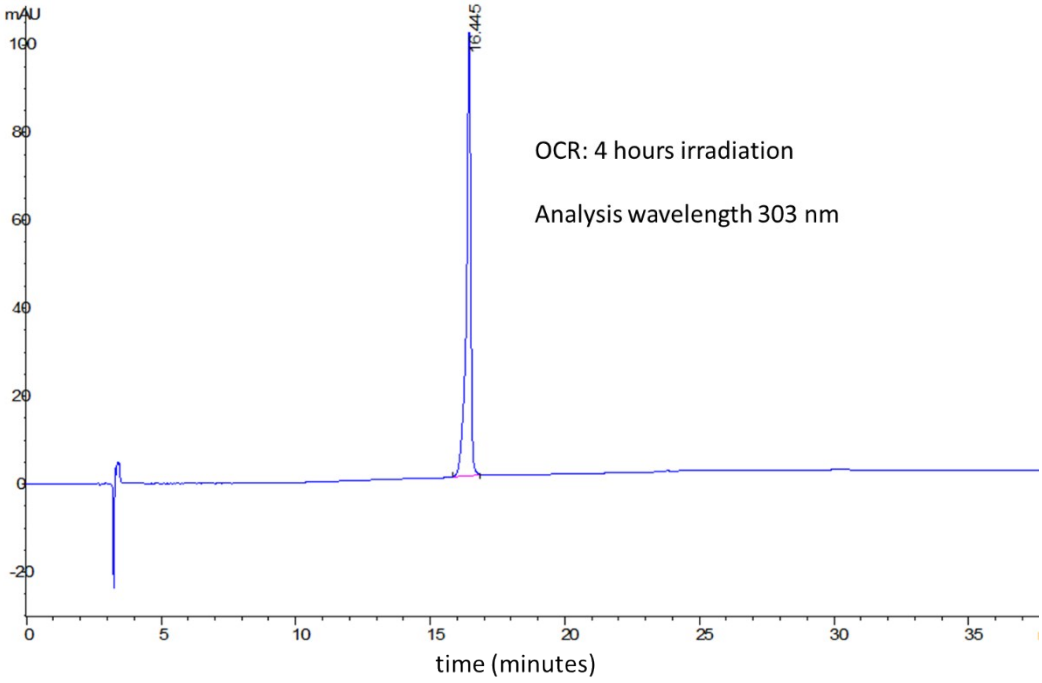
EHMC


mAU
17.167
EHMC: without irradiation
Analysis wavelength 310 nm
time (minutes)

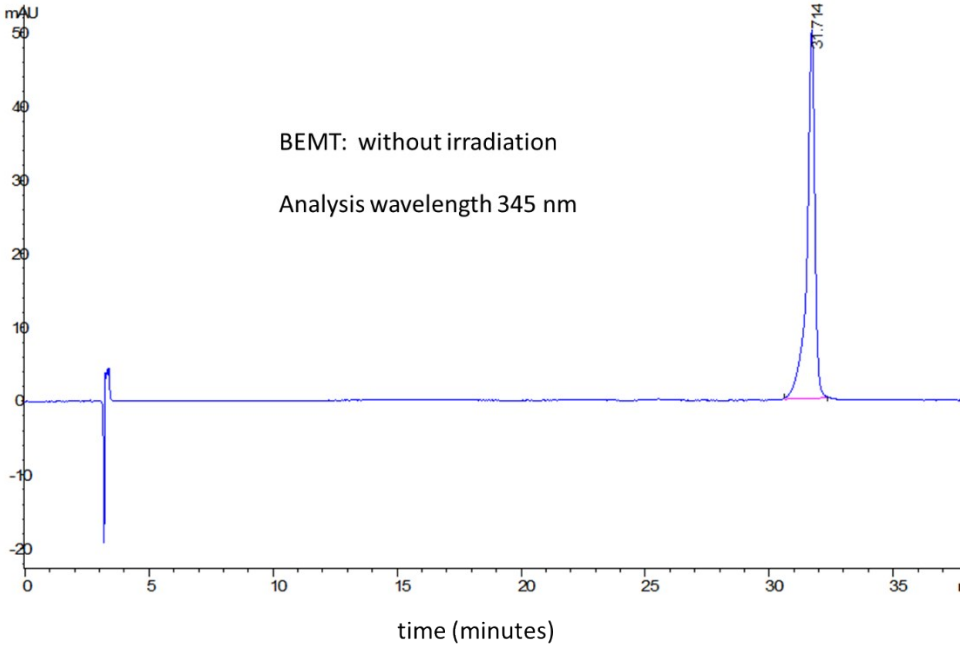

mAU
17.212
16.778
EHMC: 4 hours irradiation
Analysis wavelength 310 nm
trans-isomer
cis-isomer
time (minutes)

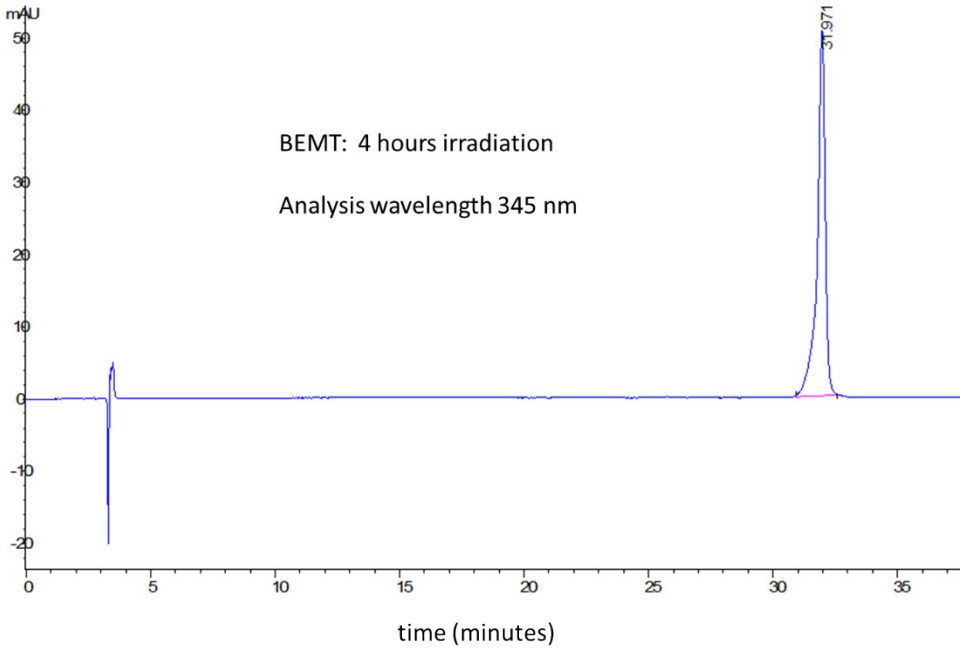
OCR


mAU
16.168
80
60
40
20
0
-20
0
5
10
15
20
25
30
35
time (minutes)
OCR: without irradiation
Analysis wavelength 303 nm


mAU
100
16.445
80
60
40
20
0
-20
0
5
10
15
20
25
30
35
time (minutes)
OCR: 4 hours irradiation
Analysis wavelength 303 nm

BEMT


mAU
50
40
30
20
10
0
-10
-20
31.714
BEMT: without irradiation
Analysis wavelength 345 nm
0
5
10
15
20
25
30
35
time (minutes)


mAU
50
40
30
20
10
0
-10
-20
31.971
BEMT: 4 hours irradiation
Analysis wavelength 345 nm
0
5
10
15
20
25
30
35
time (minutes)

TABLES WITH UV-ABSORBER CONCENTRATIONS AFTER IRRADIATION

Table S1: Experimental data of irradiation experiments starting with 2% BMDBM and different concentrations of OCR; in the table, concentrations of BMDBM in the oil phase of the emulsions are given in mol/L; N = 8, error ranges as confidence intervals (CI) with 95% level of significance

	0% OCR	3% OCR, separated (c_{OCR} = 0.308 mol/L)	3% OCR, together (c_{OCR} = 0.307 mol/L)
t (h)	**c_{BMDBM} (mol/L)**	**c_{BMDBM} (mol/L)**	**c_{BMDBM} (mol/L)**
0	0.239 ± 0.0048	0.239 ± 0.0030	0.238 ± 0.0043
1	0.072 ± 0.0044	0.121 ± 0.0054	0.190 ± 0.0037
2	0.026 ± 0.0023	0.054 ± 0.0047	0.162 ± 0.0089
4	0.005 ± 0.0024	0.011 ± 0.0022	0.102 ± 0.0064
10	0.000 ± 0.0000	0.001 ± 0.0014	0.039 ± 0.0057

	6% OCR, separated (c_{OCR} = 0.617 mol/L)	6% OCR, together (c_{OCR} = 0.612 mol/L)	9% OCR, separated (c_{OCR} = 0.925 mol/L)	9% OCR, together (c_{OCR} = 0.913 mol/L)
t (h)	**c_{BMDBM} (mol/L)**	**c_{BMDBM} (mol/L)**	**c_{BMDBM} (mol/L)**	**c_{BMDBM} (mol/L)**
0	0.239 ± 0.0034	0.237 ± 0.0030	0.237 ± 0.0041	0.236 ± 0.0038
1	0.119 ± 0.0116	0.209 ± 0.0029	0.130 ± 0.0150	0.209 ± 0.0052
2	0.066 ± 0.0102	0.186 ± 0.0014	0.075 ± 0.0146	0.195 ± 0.0038
4	0.016 ± 0.0050	0.144 ± 0.0050	0.023 ± 0.0078	0.157 ± 0.0030
10	0.003 ± 0.0006	0.079 ± 0.0049	0.004 ± 0.0011	0.099 ± 0.0085

Table S2: Experimental data of irradiation experiments starting with 2% BMDBM and different concentrations of BEMT; in the table, concentrations of BMDBM in the oil phase of the emulsions are given in mol/L; N = 8, error ranges as confidence intervals (CI) with 95% level of significance

	0% BEMT	1% BEMT, separated (c_{BEMT} = 0.059 mol/L)	1% BEMT, together (c_{BEMT} = 0.061 mol/L)
t (h)	**c_{BMDBM} (mol/L)**	**c_{BMDBM} (mol/L)**	**c_{BMDBM} (mol/L)**
0	0.239 ± 0.0048	0.239 ± 0.0042	0.247 ± 0.0036
1	0.072 ± 0.0044	0.147 ± 0.0083	0.143 ± 0.0049
2	0.026 ± 0.0023	0.087 ± 0.0118	0.089 ± 0.0038
4	0.005 ± 0.0024	0.024 ± 0.0062	0.039 ± 0.0031
10	0.000 ± 0.0000	0.004 ± 0.0006	0.005 ± 0.0048

	2% BEMT, separated (c_{BEMT} = 0.118 mol/L)	2% BEMT, together (c_{BEMT} = 0.127 mol/L)	3% BEMT, separated (c_{BEMT} = 0.178 mol/L)	3% BEMT, together (c_{BEMT} = 0.198 mol/L)
t (h)	**c_{BMDBM} (mol/L)**	**c_{BMDBM} (mol/L)**	**c_{BMDBM} (mol/L)**	**c_{BMDBM} (mol/L)**
0	0.239 ± 0.0044	0.257 ± 0.0029	0.239 ± 0.0049	0.266 ± 0.0085
1	0.154 ± 0.0120	0.176 ± 0.0063	0.162 ± 0.0142	0.204 ± 0.0100
2	0.097 ± 0.0178	0.141 ± 0.0059	0.102 ± 0.0210	0.155 ± 0.0042
4	0.039 ± 0.0105	0.090 ± 0.0040	0.038 ± 0.0121	0.112 ± 0.0069
10	0.005 ± 0.0021	0.028 ± 0.0034	0.006 ± 0.0015	0.047 ± 0.0055

Table S3: Experimental data of irradiation experiments starting with 2% EHMC and different concentrations of OCR; in the table, concentrations of EHMC in the oil phase of the emulsions are given in mol/L; N = 4, error ranges as confidence intervals (CI) with 95% level of significance

	0% OCR	3% OCR, separated (c_{OCR} = 0.287 mol/L)	3% OCR, together (c_{OCR} = 0.286 mol/L)
t (h)	**c_{EHMC} (mol/L)**	**c_{EHMC} (mol/L)**	**c_{EHMC} (mol/L)**
0	0.239 ± 0.0095	0.239 ± 0.0095	0.238 ± 0.0085
1	0 .203 ± 0.0087	0.233 ± 0.0053	0.236 ± 0.0092
2	0.177 ± 0.0104	0.229 ± 0.0043	0.230 ± 0.0097
4	0.135 ± 0.0056	0.200 ± 0.0084	0.197 ± 0.0235
10	0.074 ± 0.0102	0.133 ± 0.0098	0.163 ± 0.0065

	6% OCR, separated (c_{OCR} = 0.575 mol/L)	6% OCR, together (c_{OCR} = 0.572 mol/L)	9% OCR, separated (c_{OCR} = 0.862 mol/L)	9% OCR, together (c_{OCR} = 0.858 mol/L)
t (h)	**c_{EHMC} (mol/L)**	**c_{EHMC} (mol/L)**	**c_{EHMC} (mol/L)**	**c_{EHMC} (mol/L)**
0	0.239 ± 0.0095	0.237 ± 0.0077	0.239 ± 0.0095	0.236 ± 0.0062
1	0.247 ± 0.0112	0.231 ± 0.0180	0.252 ± 0.0077	0.244 ± 0.0192
2	0.233 ± 0.0082	0.225 ± 0.0115	0.241 ± 0.0112	0.242 ± 0.0032
4	0.214 ± 0.0120	0.230 ± 0.0241	0.226 ± 0.0112	0.228 ± 0.0028
10	0.146 ± 0.0076	0.179 ± 0.0204	0.179 ± 0.0091	0.204 ± 0.0072

Table S4: Experimental data of irradiation experiments starting with 2% EHMC and different concentrations of BEMT; in the table, concentrations of EHMC in the oil phase of the emulsions are given in mol/L; N = 4, error ranges as confidence intervals (CI) with 95% level of significance

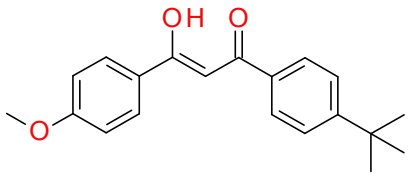
	0% BEMT	1% BEMT, separated (c_{BEMT} = 0.055 mol/L)	1% BEMT, together (c_{BEMT} = 0.057 mol/L)
t (h)	**c_{EHMC} (mol/L)**	**c_{EHMC} (mol/L)**	**c_{EHMC} (mol/L)**
0	0.239 ± 0.0095	0.239 ± 0.0095	0.246 ± 0.0057
1	0 .203 ± 0.0087	0.225 ± 0.0098	0.234 ± 0.0098
2	0.177 ± 0.0104	0.219 ± 0.0150	0.220 ± 0.0072
4	0.135 ± 0.0056	0.187 ± 0.0315	0.200 ± 0.0092
10	0.074 ± 0.0102	0.147 ± 0.0085	0.167 ± 0.0038

	2% BEMT, separated (c_{BEMT} = 0.110 mol/L)	2% BEMT, together (c_{BEMT} = 0.118 mol/L)	3% BEMT, separated (c_{BEMT} = 0.165 mol/L)	3% BEMT, together (c_{BEMT} = 0.183 mol/L)
t (h)	**c_{EHMC} (mol/L)**	**c_{EHMC} (mol/L)**	**c_{EHMC} (mol/L)**	**c_{EHMC} (mol/L)**
0	0.239 ± 0.0095	0.255 ± 0.0140	0.239 ± 0.0095	0.264 ± 0.0146
1	0.231 ± 0.0067	0.249 ± 0.0195	0.237 ± 0.0110	0.262 ± 0.0243
2	0.220 ± 0.0036	0.265 ± 0.0080	0.226 ± 0.0090	0.265 ± 0.0080
4	0.207 ± 0.0099	0.220 ± 0.0125	0.204 ± 0.0096	0.251 ± 0.0142
10	0.159 ± 0.0059	0.195 ± 0.0055	0.150 ± 0.0041	0.228 ± 0.0165

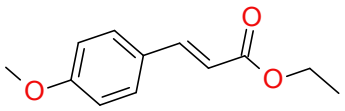
RELAXED STRUCTURES

Model compounds

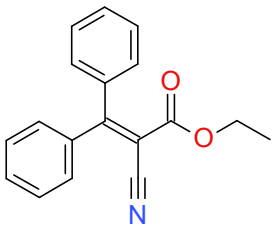
For the computations, we have used a model compounds, in which we shorten the alkyl chains:



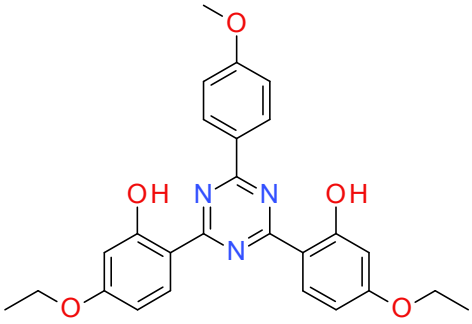
BMDBM



EHMC



OCR



BEMT

BMDBM can occur in two enol and one di-keto variant. We computed all three tautomers. The shown tautomer was lowest in energy.

BMDBM enol 1 – structure of relaxed S_0 state

45

C	2.847613	-2.073073	5.221708
C	2.444803	-2.119625	3.883410
C	2.821002	-3.237508	3.121457
C	3.564929	-4.258848	3.675781
C	3.960294	-4.194738	5.017762
C	3.595891	-3.089553	5.793272
C	1.646451	-1.000821	3.337841
O	1.321788	-0.051259	4.106434
O	4.686177	-5.238664	5.474868
C	5.117207	-5.228778	6.839968
C	1.249691	-0.990099	1.961974

C	0.501365	0.043702	1.447880
O	0.137288	1.060085	2.221264
C	0.054548	0.131720	0.052271
C	-0.561995	1.296449	-0.411376
C	-0.987725	1.402453	-1.729242
C	-0.820878	0.354170	-2.635092
C	-0.204585	-0.812387	-2.159908
C	0.224731	-0.926379	-0.851111
C	-1.278193	0.433253	-4.091360
C	-2.306042	-0.683452	-4.359894
H	-1.881608	-1.672531	-4.184235
H	-2.639453	-0.639320	-5.398993
H	-3.179629	-0.568204	-3.714841
C	-1.929085	1.780463	-4.426078
C	-0.059559	0.238354	-5.014717
H	-1.455733	2.324086	-2.042058
H	-0.705676	2.128428	0.263077
H	0.684636	-1.851603	-0.533704
H	-0.057739	-1.653470	-2.824054
H	1.545195	-1.791797	1.310571
H	2.532184	-3.322426	2.084079
H	3.851587	-5.119538	3.085820
H	3.888479	-3.015822	6.829803
H	2.565929	-1.218970	5.821542
H	0.529604	0.849345	3.135782
H	5.765882	-4.373021	7.036414
H	5.673823	-6.151175	6.979917
H	4.261414	-5.207827	7.517334
H	-0.373020	0.290255	-6.059651
H	0.685162	1.018030	-4.841563
H	0.416808	-0.729215	-4.853445
H	-2.236023	1.782372	-5.473274
H	-2.817125	1.961909	-3.817736
H	-1.236302	2.611349	-4.279863

BMDBM enol 1 – structure of relaxed S_1 state

45

C	3.463932	-2.091567	4.302338
C	2.105409	-2.354359	4.013102
C	1.512448	-3.531958	4.526456
C	2.268348	-4.454403	5.194014
C	3.642627	-4.205481	5.423920
C	4.235542	-3.007591	4.973274
C	1.277604	-1.332271	3.322472
O	0.887859	-0.621308	4.333556
O	4.292871	-5.159499	6.087032
C	5.681730	-4.999599	6.394852
C	1.021740	-1.216366	1.993507
C	0.198149	-0.186017	1.452640
O	-0.358229	0.711716	2.310182
C	-0.101791	-0.002976	0.080816

C	-0.933283	1.062539	-0.347741
C	-1.232268	1.249312	-1.684304
C	-0.737416	0.405788	-2.685003
C	0.087200	-0.651306	-2.261218
C	0.399253	-0.857343	-0.936951
C	-1.049986	0.585260	-4.169723
C	-1.752593	-0.676913	-4.706918
H	-1.129951	-1.563915	-4.584994
H	-1.976876	-0.566957	-5.771238
H	-2.689702	-0.851237	-4.174790
C	-1.965990	1.787028	-4.430564
C	0.260198	0.803454	-4.951717
H	-1.871890	2.080370	-1.946779
H	-1.337426	1.737834	0.391768
H	1.038679	-1.690072	-0.678884
H	0.497159	-1.334977	-2.994448
H	1.468760	-1.941800	1.332939
H	0.459551	-3.700814	4.352979
H	1.850078	-5.382340	5.558499
H	5.280764	-2.807445	5.152526
H	3.892221	-1.159586	3.962628
H	-0.083545	0.491301	3.218873
H	6.269186	-4.907025	5.480390
H	5.966259	-5.901449	6.927554
H	5.835392	-4.127444	7.031517
H	0.053880	0.925118	-6.018395
H	0.775157	1.698361	-4.597210
H	0.940607	-0.040937	-4.835535
H	-2.161497	1.874508	-5.501223
H	-2.926734	1.677737	-3.924239
H	-1.509313	2.720951	-4.097927

BMDBM enol 1 – structure of relaxed T_1 state

45

C	-5.133017	-5.566184	-6.808850
C	-4.553196	-4.476040	-6.136873
C	-4.390123	-3.286088	-6.861719
C	-4.786348	-3.193944	-8.188715
C	-5.362104	-4.275668	-8.859584
C	-5.523686	-5.463781	-8.130250
C	-4.153660	-4.637928	-4.732524
O	-4.339041	-5.757236	-4.136242
C	-5.806902	-4.209610	-10.320013
C	-5.028503	-5.261477	-11.134756
C	-3.555311	-3.557810	-4.016987
C	-3.135924	-3.643898	-2.645938
O	-3.319301	-4.815124	-1.993182
C	-2.542716	-2.575896	-1.947582
C	-2.303581	-1.293421	-2.539359
C	-1.723408	-0.281435	-1.826589
C	-1.342191	-0.473317	-0.481513

C	-1.564283	-1.721707	0.128725
C	-2.147383	-2.742096	-0.583939
O	-0.778775	0.585377	0.130719
C	-0.366087	0.458373	1.497437
C	-7.315451	-4.514336	-10.406144
C	-5.556191	-2.832151	-10.945002
H	-7.548244	-5.505949	-10.016439
H	-7.644971	-4.475218	-11.446882
H	-7.890954	-3.781245	-9.836953
H	-4.637316	-2.253684	-8.699008
H	-3.951231	-2.411665	-6.402207
H	-5.270529	-6.495524	-6.273798
H	-5.965002	-6.329919	-8.606050
H	-3.403352	-2.620163	-4.522497
H	-2.312696	-3.696117	-0.105741
H	-1.280490	-1.890097	1.157074
H	-1.546594	0.684170	-2.282264
H	-2.580396	-1.104659	-3.565748
H	-1.219606	0.231425	2.138269
H	0.052775	1.423067	1.768384
H	0.393911	-0.317938	1.599792
H	-5.341139	-5.229316	-12.180925
H	-3.954899	-5.066182	-11.091996
H	-5.205536	-6.270773	-10.761265
H	-5.891382	-2.840607	-11.983574
H	-6.105418	-2.045957	-10.423376
H	-4.495890	-2.572391	-10.938763
H	-3.745621	-5.426687	-2.663546

BMDBM enol 2 – structure of relaxed S_0 state

45

C	-5.07743	-5.54759	-6.80772
C	-4.65535	-4.40117	-6.12339
C	-4.60833	-3.19734	-6.82868
C	-4.97030	-3.14154	-8.16910
C	-5.38443	-4.28161	-8.85987
C	-5.42772	-5.48650	-8.14401
C	-4.28918	-4.51199	-4.68898
O	-4.57412	-5.57780	-4.07252
C	-5.78353	-4.25817	-10.33539
C	-4.85807	-5.20536	-11.12396
C	-3.61721	-3.43874	-4.03057
C	-3.27137	-3.52761	-2.69812
O	-3.56115	-4.62396	-2.00712
C	-2.57887	-2.48081	-1.94740
C	-2.27619	-1.23210	-2.51698
C	-1.62115	-0.26109	-1.79171
C	-1.24288	-0.50563	-0.46420
C	-1.53579	-1.74023	0.11994
C	-2.19696	-2.70824	-0.62108
O	-0.60528	0.50399	0.16735

C	-0.19715	0.31275	1.52613
C	-7.24159	-4.73806	-10.47256
C	-5.67600	-2.85646	-10.94746
H	-7.36856	-5.75383	-10.09644
H	-7.53870	-4.72820	-11.52355
H	-7.91798	-4.08302	-9.91945
H	-4.92541	-2.18615	-8.67042
H	-4.30563	-2.28252	-6.33919
H	-5.12135	-6.48884	-6.27737
H	-5.74094	-6.39600	-8.63926
H	-3.35584	-2.55432	-4.58221
H	-2.41782	-3.66036	-0.16065
H	-1.25531	-1.95483	1.13997
H	-1.39215	0.70007	-2.23287
H	-2.55914	-1.01024	-3.53596
H	-1.05982	0.12328	2.16767
H	0.28442	1.24032	1.82259
H	0.51213	-0.51325	1.60588
H	-5.13367	-5.19938	-12.18076
H	-3.81679	-4.88720	-11.03991
H	-4.93042	-6.23179	-10.76270
H	-5.97070	-2.89808	-11.99734
H	-6.33314	-2.14446	-10.44451
H	-4.65492	-2.47294	-10.90243
H	-4.01999	-5.24386	-2.67012

BMDBM enol 2 – structure of relaxed S_1 state

45

C	-5.12579	-5.55713	-6.80666
C	-4.54054	-4.44574	-6.14023
C	-4.38946	-3.25417	-6.89891
C	-4.79302	-3.18873	-8.21826
C	-5.36908	-4.28521	-8.87361
C	-5.51977	-5.46960	-8.11805
C	-4.14220	-4.58175	-4.77287
O	-4.29405	-5.67059	-4.12530
C	-5.82365	-4.24755	-10.32823
C	-5.05055	-5.31048	-11.13597
C	-3.53225	-3.45247	-4.04691
C	-3.12930	-3.58088	-2.71485
O	-3.29631	-4.73488	-2.08345
C	-2.52244	-2.50779	-1.96159
C	-2.28562	-1.21851	-2.50545
C	-1.70545	-0.22853	-1.75575
C	-1.33117	-0.47507	-0.42197
C	-1.55564	-1.74370	0.13989
C	-2.13940	-2.73432	-0.61950
O	-0.77007	0.55805	0.23013
C	-0.36245	0.38979	1.58485
C	-7.33311	-4.55678	-10.40386
C	-5.58237	-2.88184	-10.98213

H	-7.56340	-5.53734	-9.98656
H	-7.67114	-4.54558	-11.44329
H	-7.90682	-3.81294	-9.84797
H	-4.65321	-2.25651	-8.74681
H	-3.95204	-2.37028	-6.45609
H	-5.25229	-6.47597	-6.25184
H	-5.96013	-6.34310	-8.58221
H	-3.39485	-2.51065	-4.54587
H	-2.31487	-3.71167	-0.19475
H	-1.27543	-1.95220	1.16168
H	-1.52376	0.75503	-2.16739
H	-2.56319	-1.00060	-3.52627
H	-1.21521	0.14199	2.22141
H	0.05519	1.34583	1.88789
H	0.39972	-0.38854	1.66954
H	-5.37457	-5.30354	-12.17987
H	-3.97790	-5.11032	-11.10780
H	-5.21436	-6.31312	-10.74022
H	-5.92330	-2.90681	-12.01883
H	-6.13045	-2.08788	-10.47139
H	-4.52298	-2.61873	-10.98731
H	-3.74312	-5.35004	-2.80372

BMDBM enol 2 – structure of relaxed T_1 state

45

C	-5.13302	-5.56618	-6.80885
C	-4.55320	-4.47604	-6.13687
C	-4.39012	-3.28609	-6.86172
C	-4.78635	-3.19394	-8.18871
C	-5.36210	-4.27567	-8.85958
C	-5.52369	-5.46378	-8.13025
C	-4.15366	-4.63793	-4.73252
O	-4.33904	-5.75724	-4.13624
C	-5.80690	-4.20961	-10.32001
C	-5.02850	-5.26148	-11.13476
C	-3.55531	-3.55781	-4.01699
C	-3.13592	-3.64390	-2.64594
O	-3.31930	-4.81512	-1.99318
C	-2.54272	-2.57590	-1.94758
C	-2.30358	-1.29342	-2.53936
C	-1.72341	-0.28144	-1.82659
C	-1.34219	-0.47332	-0.48151
C	-1.56428	-1.72171	0.12872
C	-2.14738	-2.74210	-0.58394
O	-0.77878	0.58538	0.13072
C	-0.36609	0.45837	1.49744
C	-7.31545	-4.51434	-10.40614
C	-5.55619	-2.83215	-10.94500
H	-7.54824	-5.50595	-10.01644
H	-7.64497	-4.47522	-11.44688
H	-7.89095	-3.78124	-9.83695

H	-4.63732	-2.25368	-8.69901
H	-3.95123	-2.41166	-6.40221
H	-5.27053	-6.49552	-6.27380
H	-5.96500	-6.32992	-8.60605
H	-3.40335	-2.62016	-4.52250
H	-2.31270	-3.69612	-0.10574
H	-1.28049	-1.89010	1.15707
H	-1.54659	0.68417	-2.28226
H	-2.58040	-1.10466	-3.56575
H	-1.21961	0.23142	2.13827
H	0.05278	1.42307	1.76838
H	0.39391	-0.31794	1.59979
H	-5.34114	-5.22932	-12.18093
H	-3.95490	-5.06618	-11.09200
H	-5.20554	-6.27077	-10.76126
H	-5.89138	-2.84061	-11.98357
H	-6.10542	-2.04596	-10.42338
H	-4.49589	-2.57239	-10.93876
H	-3.74562	-5.42669	-2.66355

BMDBM keto – structure of relaxed S_0 state

45

C	0.91540	4.44956	1.91508
C	1.72649	3.62107	1.11967
C	2.81170	2.97793	1.72234
C	3.09058	3.14572	3.07070
C	2.26888	3.96727	3.84688
C	1.17482	4.61885	3.25547
C	1.40728	3.46874	-0.31069
O	0.56753	4.16991	-0.85781
O	2.44862	4.19266	5.16401
C	3.54441	3.55266	5.82858
C	2.14504	2.40347	-1.11997
C	1.90965	0.97448	-0.64114
O	2.85002	0.30217	-0.24684
C	0.53191	0.43357	-0.66110
C	0.26386	-0.77064	0.00424
C	-1.01010	-1.30248	0.00955
C	-2.07228	-0.66816	-0.65432
C	-1.79455	0.52617	-1.32027
C	-0.51740	1.07394	-1.32242
C	-3.46571	-1.29466	-0.62449
C	-3.39923	-2.70117	-1.25169
H	-3.06505	-2.64656	-2.28987
H	-4.38939	-3.16142	-1.23441
H	-2.71508	-3.35319	-0.70764
C	-3.93502	-1.40960	0.83923
C	-4.49650	-0.46626	-1.40007
H	-1.18385	-2.22852	0.54087
H	1.06798	-1.27514	0.52261
H	-0.35112	2.00134	-1.85065

H	-2.57604	1.04950	-1.85051
H	1.81738	2.50202	-2.15429
H	3.46200	2.33903	1.14315
H	3.94068	2.64012	3.50259
H	0.54663	5.24852	3.87193
H	0.07251	4.95083	1.45938
H	3.45046	2.46672	5.77223
H	3.48782	3.87376	6.86473
H	4.49614	3.86605	5.39588
H	3.21834	2.58502	-1.07979
H	-5.46883	-0.95848	-1.34479
H	-4.60604	0.53640	-0.98253
H	-4.22947	-0.37281	-2.45438
H	-4.92980	-1.85878	0.87473
H	-3.26277	-2.03245	1.43014
H	-3.98714	-0.42444	1.30742

BMDBM keto – structure of relaxed S_1 state

45

C	1.04602	4.58365	1.62761
C	1.79612	3.61201	0.94281
C	2.67507	2.80675	1.67191
C	2.80841	2.95835	3.04295
C	2.05270	3.92590	3.71033
C	1.16779	4.73852	2.98862
C	1.63556	3.50722	-0.51088
O	0.97272	4.29242	-1.16258
O	2.10538	4.14938	5.04055
C	2.97345	3.35154	5.83582
C	2.31906	2.39016	-1.31178
C	1.94853	0.98845	-0.80808
O	3.02944	0.37441	-0.49061
C	0.64702	0.48604	-0.72606
C	0.41881	-0.81445	-0.18170
C	-0.85192	-1.32811	-0.10157
C	-1.98279	-0.61982	-0.54985
C	-1.75409	0.65287	-1.09488
C	-0.49306	1.20168	-1.18886
C	-3.37095	-1.24433	-0.43311
C	-3.41220	-2.56273	-1.23125
H	-3.20390	-2.38053	-2.28717
H	-4.39879	-3.02585	-1.15071
H	-2.67535	-3.27752	-0.86357
C	-3.67923	-1.54104	1.04804
C	-4.47142	-0.32393	-0.97454
H	-0.97636	-2.31594	0.32432
H	1.26110	-1.39126	0.17504
H	-0.38328	2.18310	-1.62571
H	-2.58462	1.23828	-1.46251
H	2.03311	2.48923	-2.36071
H	3.25825	2.04154	1.18155

H	3.49362	2.31988	3.57947
H	0.58962	5.47802	3.52597
H	0.36408	5.20564	1.06453
H	2.70246	2.29436	5.77603
H	2.84630	3.70225	6.85658
H	4.01578	3.48000	5.53266
H	3.40095	2.52429	-1.24113
H	-5.44198	-0.81212	-0.86860
H	-4.51308	0.62004	-0.42807
H	-4.32615	-0.10084	-2.03312
H	-4.66738	-1.99719	1.14743
H	-2.94911	-2.22610	1.48037
H	-3.66492	-0.62151	1.63618

BMDBM keto – structure of relaxed T_1 state

45

C	1.07301	4.57625	2.27535
C	1.75740	3.60643	1.43999
C	2.96155	2.98764	1.97835
C	3.44290	3.33336	3.20128
C	2.76041	4.30639	3.99149
C	1.55903	4.91151	3.49299
C	1.24256	3.33276	0.13202
O	0.19180	3.91811	-0.27082
O	3.14852	4.70947	5.20004
C	4.34054	4.16230	5.79426
C	1.93208	2.31360	-0.76367
C	1.62774	0.91376	-0.25887
O	2.48920	0.28461	0.35092
C	0.27077	0.35093	-0.45633
C	-0.04221	-0.88810	0.12150
C	-1.28921	-1.45533	-0.05289
C	-2.28458	-0.82011	-0.81210
C	-1.96604	0.41194	-1.38430
C	-0.71368	0.99096	-1.21269
C	-3.65053	-1.48495	-0.98021
C	-3.46515	-2.85897	-1.65344
H	-3.01108	-2.74782	-2.64037
H	-4.43470	-3.34688	-1.77563
H	-2.82996	-3.51636	-1.05885
C	-4.29180	-1.67961	0.40791
C	-4.60558	-0.64961	-1.84088
H	-1.49399	-2.41139	0.41048
H	0.70954	-1.39562	0.71080
H	-0.51865	1.95333	-1.66143
H	-2.69661	0.94213	-1.97725
H	1.56651	2.46051	-1.77828
H	3.47267	2.23455	1.40032
H	4.34129	2.86399	3.57484
H	1.05893	5.63826	4.12028
H	0.17052	5.02775	1.89310

H	4.23337	3.08608	5.92763
H	4.43388	4.65274	6.75763
H	5.20658	4.38529	5.17156
H	3.01501	2.43822	-0.75913
H	-5.56101	-1.16976	-1.92775
H	-4.79794	0.32915	-1.39737
H	-4.21451	-0.49943	-2.84893
H	-5.26871	-2.15650	0.30219
H	-3.67689	-2.31031	1.05082
H	-4.43221	-0.71857	0.90719

EHMC – structure of relaxed S_0 state

29

C	-0.657195	-7.916126	3.159846
C	0.143337	-8.589689	2.236282
C	0.751927	-7.874748	1.193027
C	0.562570	-6.515448	1.078724
C	-0.240315	-5.814134	1.998295
C	-0.838303	-6.545539	3.030615
O	0.389203	-9.919752	2.264933
C	-0.205113	-10.701254	3.305622
C	-0.472438	-4.384264	1.924420
C	0.013812	-3.522866	1.015394
C	-0.316631	-2.097227	1.078295
O	-1.026697	-1.559679	1.911348
O	0.272274	-1.418596	0.076790
C	0.030799	0.009500	0.016502
H	-1.294646	-10.652063	3.254869
H	0.134389	-10.364410	4.287139
H	0.124609	-11.722104	3.133715
H	1.369508	-8.411513	0.484521
H	1.043365	-5.988647	0.265143
H	-1.460837	-6.028593	3.750909
H	-1.137052	-8.441550	3.971644
H	-1.114652	-3.974710	2.698456
H	0.661563	-3.832599	0.206572
C	0.784250	0.550352	-1.175217
H	-1.043419	0.175356	-0.072197
H	0.371511	0.457732	0.950508
H	0.621576	1.627214	-1.246599
H	1.855945	0.370978	-1.074518
H	0.435925	0.088431	-2.100500

EHMC – structure of relaxed S_1 state

29

C	-0.684243	-7.915336	3.190794
C	0.145727	-8.545624	2.224817

C	0.736262	-7.783031	1.204906
C	0.521555	-6.427255	1.126939
C	-0.316587	-5.757258	2.092456
C	-0.899704	-6.564371	3.115022
O	0.417845	-9.864727	2.213957
C	-0.140915	-10.709593	3.213193
C	-0.565546	-4.362553	2.049371
C	-0.030336	-3.517150	1.076258
C	-0.317195	-2.103793	1.083927
O	-1.020351	-1.523843	1.902633
O	0.298342	-1.455224	0.047569
C	0.070667	-0.042252	-0.025197
H	-1.233290	-10.697064	3.171380
H	0.192132	-10.410685	4.210671
H	0.222106	-11.709275	2.990782
H	1.362946	-8.294177	0.485755
H	0.985078	-5.857060	0.336311
H	-1.531694	-6.080699	3.849288
H	-1.144476	-8.490074	3.980509
H	-1.201982	-3.919780	2.804559
H	0.611918	-3.886374	0.289354
C	0.825574	0.485232	-1.224775
H	-1.003330	0.143531	-0.106573
H	0.408193	0.423017	0.904455
H	0.675845	1.563258	-1.313531
H	1.895393	0.293623	-1.126458
H	0.475093	0.012597	-2.143838

EHMC – structure of relaxed T_1 state

29

C	-0.680349	-7.922285	3.193059
C	0.140768	-8.562979	2.233030
C	0.732178	-7.798777	1.200245
C	0.524191	-6.453720	1.115270
C	-0.307932	-5.759683	2.076500
C	-0.894744	-6.576315	3.116540
O	0.412401	-9.880508	2.223051
C	-0.153306	-10.718776	3.239896
C	-0.552745	-4.399937	2.039703
C	-0.016179	-3.502969	1.048651
C	-0.309449	-2.100868	1.066290
O	-1.023117	-1.533202	1.894647
O	0.294954	-1.434703	0.048093
C	0.063533	-0.011112	-0.024688
H	-1.243080	-10.695959	3.194676
H	0.186821	-10.407107	4.228530
H	0.204477	-11.721406	3.025255
H	1.355708	-8.309918	0.477560
H	0.991098	-5.900529	0.313763
H	-1.522970	-6.091688	3.853118
H	-1.139949	-8.490703	3.988309

H	-1.188493	-3.967890	2.801713
H	0.626993	-3.861351	0.258655
C	0.823377	0.517075	-1.218911
H	-1.009367	0.166091	-0.118008
H	0.403249	0.448019	0.905403
H	0.668007	1.594371	-1.300202
H	1.893752	0.331514	-1.114119
H	0.475204	0.049378	-2.141493

OCR – structure of relaxed S_0 state

36

C	-0.855298	0.717702	8.417743
C	-0.881187	0.056061	7.198894
C	-0.052042	0.471611	6.148883
C	0.827735	1.539890	6.359134
C	0.868579	2.184188	7.587366
C	0.021509	1.781261	8.615814
C	-0.090161	-0.236475	4.857847
C	-0.108002	0.442671	3.672709
C	-0.163320	-1.706627	4.913097
C	0.680513	-2.417450	5.773215
C	0.606668	-3.801767	5.841489
C	-0.334995	-4.488291	5.080000
C	-1.199866	-3.785070	4.245034
C	-1.110502	-2.404184	4.156649
C	-0.345945	1.845074	3.632100
N	-0.557488	2.977676	3.562027
C	0.126770	-0.203032	2.343681
O	-0.510025	0.451344	1.372614
C	-0.300858	-0.017485	0.010848
C	-1.073254	0.897610	-0.906748
O	0.836064	-1.166472	2.164673
H	-1.513975	0.400238	9.215647
H	-1.557476	-0.774755	7.049370
H	1.502198	1.843735	5.570391
H	1.565823	2.997021	7.743918
H	0.050813	2.288475	9.571704
H	1.405980	-1.884177	6.373144
H	1.277777	-4.344340	6.494685
H	-0.402364	-5.566798	5.144849
H	-1.946961	-4.313399	3.666912
H	-1.792677	-1.858645	3.517924
H	-0.647819	-1.049012	-0.050214
H	0.769489	0.002540	-0.193801
H	-2.139496	0.872836	-0.677002
H	-0.935963	0.568827	-1.938227
H	-0.717607	1.925523	-0.822814

OCR – structure of relaxed S_1 state

36

C	-0.191599	0.091788	8.584301
C	-0.224676	-0.353756	7.279117
C	-0.172933	0.548550	6.176888
C	-0.085576	1.931828	6.502914
C	-0.053575	2.359240	7.814480
C	-0.105593	1.453325	8.874297
C	-0.207676	0.077422	4.839666
C	-0.166594	0.813839	3.616662
C	-0.300619	-1.407427	4.603180
C	0.882415	-2.219180	4.755483
C	0.789184	-3.570899	4.933122
C	-0.471254	-4.186593	5.015811
C	-1.646688	-3.420081	4.942459
C	-1.573608	-2.067081	4.765034
C	-0.080695	2.208024	3.436582
N	-0.010611	3.348121	3.252035
C	-0.222692	-0.016802	2.484379
O	-0.194772	0.510484	1.271089
C	-0.255552	-0.384891	0.134577
C	-0.207709	0.472167	-1.107166
O	-0.300652	-1.280222	2.629209
H	-0.233399	-0.630591	9.390371
H	-0.291720	-1.417632	7.105214
H	-0.042988	2.668910	5.717834
H	0.013345	3.421246	8.016368
H	-0.079905	1.798953	9.898752
H	1.840991	-1.722858	4.712173
H	1.684473	-4.170940	5.026022
H	-0.536906	-5.257191	5.154944
H	-2.608498	-3.904977	5.042407
H	-2.463858	-1.456111	4.728720
H	-1.176966	-0.965532	0.197383
H	0.587313	-1.075236	0.189477
H	-1.051372	1.162302	-1.135199
H	-0.250829	-0.164819	-1.992480
H	0.714432	1.052923	-1.142550

OCR – structure of relaxed T_1 state

36

C	0.335467	0.828076	8.377831
C	-0.115627	-0.033103	7.394259
C	-0.039265	0.317597	6.027522
C	0.485339	1.591022	5.713253
C	0.940029	2.443274	6.702247
C	0.874558	2.067822	8.041931
C	-0.532547	-0.551144	4.991498

C	-0.899267	0.058448	3.695580
C	-0.680180	-1.985264	5.102365
C	0.154280	-2.750086	5.944707
C	0.028863	-4.126211	6.013041
C	-0.926195	-4.789335	5.246409
C	-1.746119	-4.055601	4.393627
C	-1.621653	-2.679695	4.313628
C	-2.186075	0.556940	3.507712
N	-3.272506	0.955763	3.395828
C	0.094574	0.114429	2.603636
O	-0.414523	0.652190	1.485800
C	0.482177	0.747917	0.354405
C	-0.288516	1.372391	-0.783807
O	1.230034	-0.281765	2.726422
H	0.253358	0.537913	9.417674
H	-0.570395	-0.971334	7.676086
H	0.555949	1.898657	4.679006
H	1.350055	3.407251	6.429344
H	1.226916	2.738031	8.814951
H	0.931429	-2.256336	6.509274
H	0.691442	-4.689553	6.657905
H	-1.021897	-5.865672	5.304165
H	-2.488905	-4.559880	3.788775
H	-2.278563	-2.129192	3.653945
H	0.839481	-0.254231	0.112373
H	1.345217	1.347533	0.648299
H	-1.149992	0.760419	-1.053393
H	0.358870	1.461105	-1.658034
H	-0.643175	2.367930	-0.514705

BEMT – structure of relaxed S_0 state

59

N	0.799689	5.843575	3.747642
C	0.950409	6.977719	4.436171
N	0.908527	8.179038	3.854335
C	0.702898	8.216399	2.519236
N	0.546254	7.118268	1.775462
C	0.599647	5.947215	2.414925
C	0.659263	9.520754	1.873677
C	1.169932	6.900563	5.883907
C	0.429086	4.717072	1.654970
C	0.860857	10.724760	2.590998
C	0.813810	11.957966	1.937839
C	0.566321	12.012338	0.571701
C	0.363717	10.825963	-0.158705
C	0.412942	9.618023	0.490053
C	0.975092	8.018671	6.698469
C	1.172655	7.957100	8.069100
C	1.586447	6.756089	8.652734
C	1.790635	5.628034	7.846874
C	1.579359	5.701219	6.486556

C	0.428883	3.442625	2.272080
C	0.258923	2.284281	1.511175
C	0.089291	2.374942	0.135147
C	0.087104	3.633105	-0.496578
C	0.252895	4.766769	0.258155
O	1.812201	6.591373	9.973782
C	1.626906	7.711453	10.846296
H	1.867420	7.351516	11.842637
H	0.592097	8.057816	10.818749
H	2.298559	8.528606	10.576670
O	0.503290	13.157282	-0.137518
O	1.110431	10.742315	3.913340
O	0.582662	3.285087	3.599710
O	-0.081093	1.310475	-0.674606
C	0.701021	14.413428	0.539446
C	0.575721	15.512772	-0.488385
C	-0.093922	-0.011376	-0.102065
C	-0.302945	-0.996349	-1.227625
H	0.975479	12.847748	2.526721
H	0.172144	10.887668	-1.221275
H	0.259063	8.702616	-0.062822
H	0.641041	8.949198	6.262921
H	0.999895	8.838085	8.668245
H	2.118813	4.706335	8.309004
H	1.755843	4.825903	5.878516
H	0.263820	1.336163	2.026654
H	-0.045852	3.684023	-1.568642
H	0.251673	5.736492	-0.218271
H	1.690627	14.415434	1.003295
H	-0.052416	14.516815	1.324323
H	-0.413571	15.503362	-0.948711
H	1.329082	15.401657	-1.269880
H	0.721455	16.479725	-0.004096
H	-0.900322	-0.072502	0.633033
H	0.856736	-0.187404	0.407484
H	0.504453	-0.928240	-1.958441
H	-1.252304	-0.812626	-1.733192
H	-0.317889	-2.010025	-0.823850
H	0.686507	4.205965	3.980900
H	1.110955	9.785424	4.211033

BEMT – structure of relaxed S_1 state

59

N	0.780731	5.867640	3.746490
C	0.925251	7.015224	4.544091
N	0.873852	8.200401	3.884316
C	0.678730	8.240162	2.588486
N	0.505336	7.096492	1.796969
C	0.573627	5.967283	2.428399
C	0.639397	9.515915	1.910980
C	1.110221	6.915817	5.937984

C	0.416456	4.687103	1.666184
C	0.836742	10.736646	2.609480
C	0.791569	11.955105	1.930890
C	0.550033	11.981339	0.563361
C	0.353037	10.784271	-0.145557
C	0.399669	9.587120	0.524006
C	1.197346	8.077192	6.749022
C	1.384459	7.997990	8.113869
C	1.494429	6.752213	8.741699
C	1.406421	5.590387	7.965517
C	1.219399	5.662360	6.605812
C	0.464971	3.377177	2.302898
C	0.298848	2.216412	1.459749
C	0.102643	2.332520	0.101226
C	0.063005	3.610851	-0.480508
C	0.220440	4.757100	0.312400
O	1.681631	6.569717	10.079539
C	1.776034	7.716969	10.903822
H	1.924029	7.349251	11.916576
H	0.859242	8.313508	10.865176
H	2.625464	8.345283	10.618387
O	0.487711	13.115608	-0.171290
O	1.077704	10.770486	3.924124
O	0.643109	3.219963	3.535485
O	-0.060300	1.299507	-0.754183
C	0.677508	14.373825	0.477122
C	0.554172	15.454456	-0.573137
C	-0.031085	-0.032648	-0.231477
C	-0.235002	-0.984624	-1.387032
H	0.950058	12.852566	2.508239
H	0.167126	10.833374	-1.209229
H	0.249563	8.659791	-0.007382
H	1.097186	9.051012	6.294585
H	1.440864	8.912944	8.685261
H	1.490671	4.631820	8.460206
H	1.164638	4.733365	6.055731
H	0.339786	1.264781	1.966080
H	-0.090389	3.692826	-1.547065
H	0.188139	5.733301	-0.149300
H	1.664808	14.394878	0.949886
H	-0.077403	14.497655	1.260349
H	-0.431111	15.427446	-1.040150
H	1.308582	15.324732	-1.350053
H	0.693689	16.435296	-0.115098
H	-0.821543	-0.143679	0.517724
H	0.931613	-0.206435	0.259848
H	0.555558	-0.866106	-2.128751
H	-1.195129	-0.803702	-1.871374
H	-0.218461	-2.013918	-1.025150
H	0.799735	4.921010	4.121833
H	1.077408	9.819686	4.232219

BEMT – structure of relaxed T_1 state

59

N	0.788949	5.815906	3.761591
C	0.914410	6.969065	4.482538
N	0.852835	8.193581	3.879168
C	0.677122	8.219179	2.556813
N	0.536548	7.112955	1.796730
C	0.594972	5.929387	2.448475
C	0.635429	9.521218	1.892203
C	1.112107	6.898129	5.883824
C	0.434057	4.705648	1.664675
C	0.824355	10.731104	2.599571
C	0.782916	11.959923	1.937890
C	0.550546	12.003587	0.567954
C	0.360068	10.812504	-0.153103
C	0.405112	9.607092	0.507453
C	1.135353	8.100692	6.706734
C	1.331713	8.035817	8.051368
C	1.521839	6.776717	8.681781
C	1.500520	5.576685	7.891925
C	1.301504	5.631405	6.553821
C	0.430997	3.425408	2.265747
C	0.271481	2.273357	1.493479
C	0.116471	2.376927	0.115740
C	0.117324	3.639533	-0.500841
C	0.272676	4.768695	0.269028
O	1.724215	6.597183	9.985806
C	1.766236	7.734535	10.867392
H	1.944961	7.326921	11.856933
H	0.813441	8.263118	10.842960
H	2.579233	8.401296	10.580673
O	0.492343	13.146806	-0.151538
O	1.059121	10.750978	3.926431
O	0.571601	3.264107	3.596353
O	-0.041920	1.316018	-0.707626
C	0.678209	14.405281	0.520878
C	0.561589	15.500104	-0.513253
C	-0.054543	-0.008331	-0.145355
C	-0.244660	-0.987134	-1.280066
H	0.935573	12.854493	2.522207
H	0.180122	10.863864	-1.218453
H	0.259972	8.686718	-0.039484
H	0.966832	9.057226	6.240352
H	1.335384	8.944940	8.634639
H	1.654037	4.632434	8.397735
H	1.310439	4.722849	5.973952
H	0.273689	1.320215	1.999973
H	-0.004115	3.702590	-1.573838
H	0.274056	5.743301	-0.197248
H	1.662310	14.414265	0.996829
H	-0.084151	14.511744	1.297067
H	-0.422195	15.485376	-0.985239

H	1.324193	15.387640	-1.285616
H	0.698639	16.469987	-0.032227
H	-0.869150	-0.080862	0.580040
H	0.890564	-0.184860	0.374837
H	0.571011	-0.909314	-2.000751
H	-1.188763	-0.804893	-1.796023
H	-0.258912	-2.003917	-0.884066
H	0.671800	4.190706	3.972927
H	1.051753	9.788766	4.217521