Supplementary Information

Triplet Stabilization for the Enhanced Drug Photorelease from Sunscreen-Based Photocages

Mauricio Lineros-Rosa, M. Consuelo Cuquerella, Antonio Francés-Monerris, Antonio Monari*, Miguel A. Miranda* and Virginie Lhiaubet-Vallet*

Index:

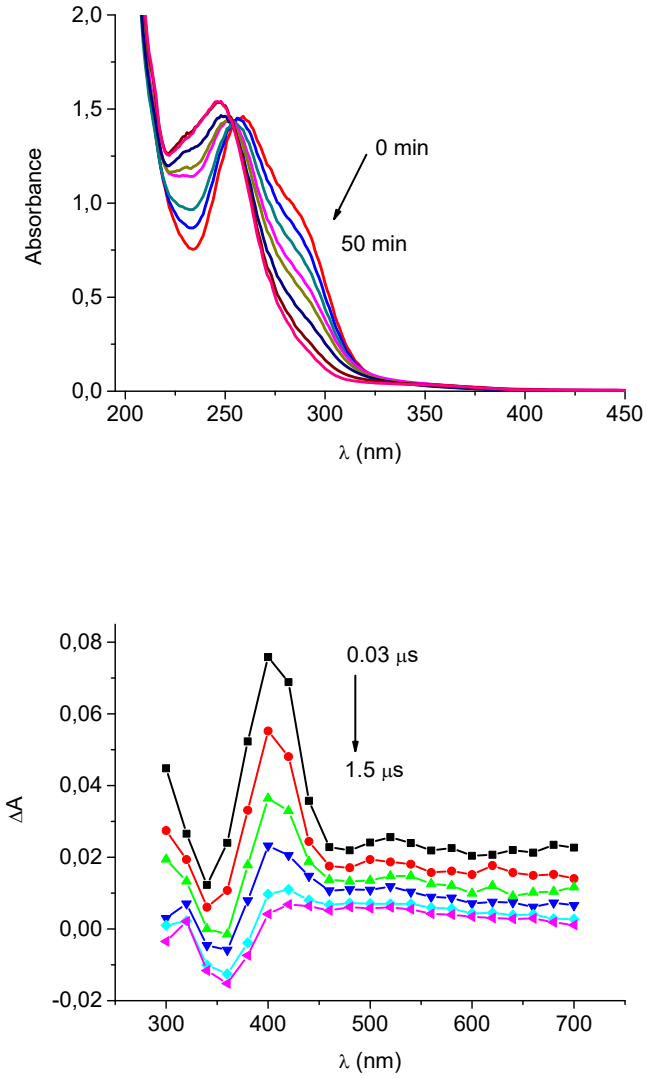

Figure S1. UV absorption changes for AB–KP in deaerated acetonitrile under SSL irradiation (up). Transient absorption spectra of AB-KP in acetonitrile under N_2, at different times after the 355 nm laser pulse (down)

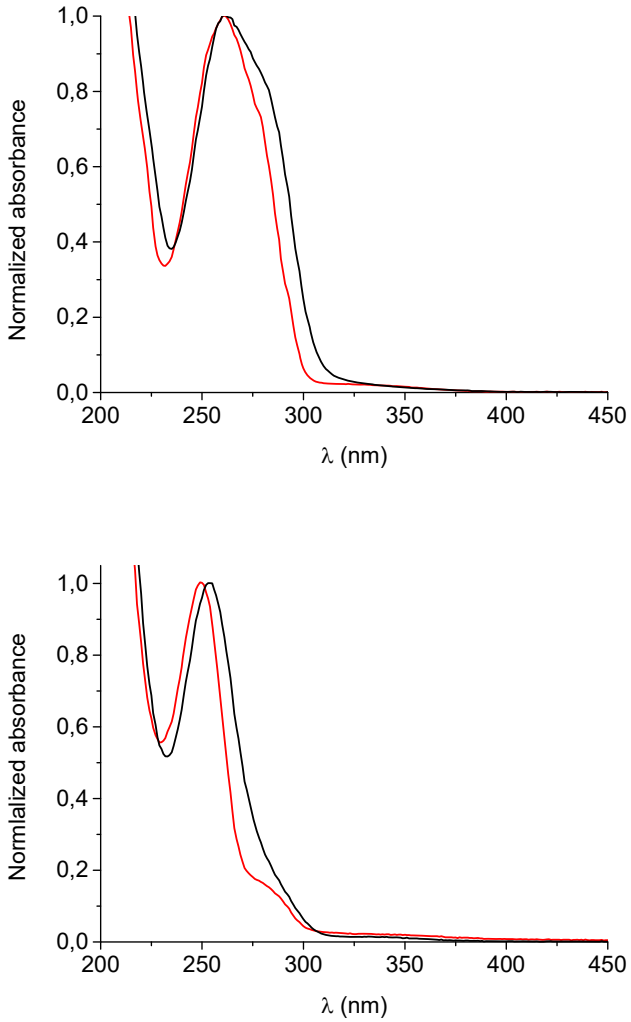

Figure S2. (up) Normalized UV-Vis absorption spectra of AB-Me in hexane (red) and ethanol (black), (bottom) Normalized UV-Vis absorption spectra of KP-Me in hexane (red) and ethanol (black)

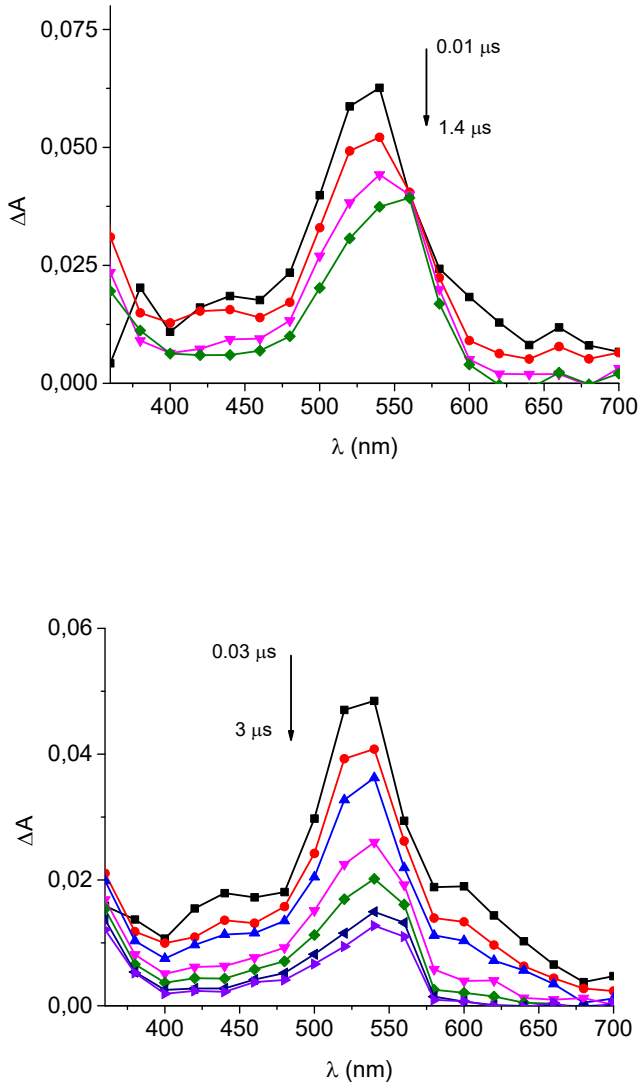

Figure S3. Transient absorption spectra of KP-Me in ethanol (up), or hexane (bottom) at different time after the 355 nm laser pulse

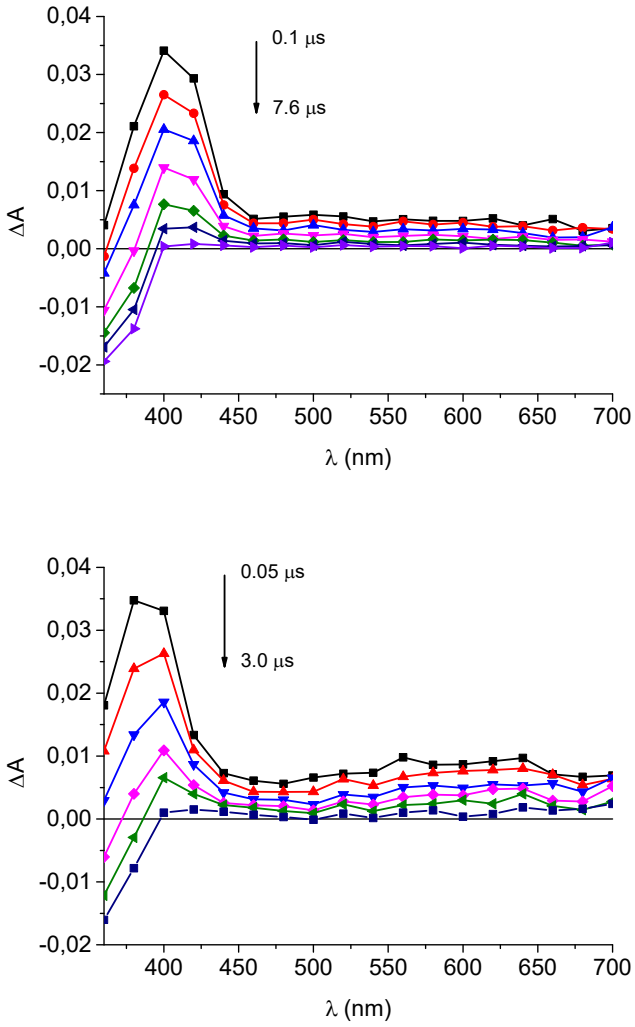

Figure S4. Transient absorption spectra of an AB-Me solution of 2 mM in ethanol (up), or 1.5 mM in hexane (bottom) at different time after the 355 nm laser pulse

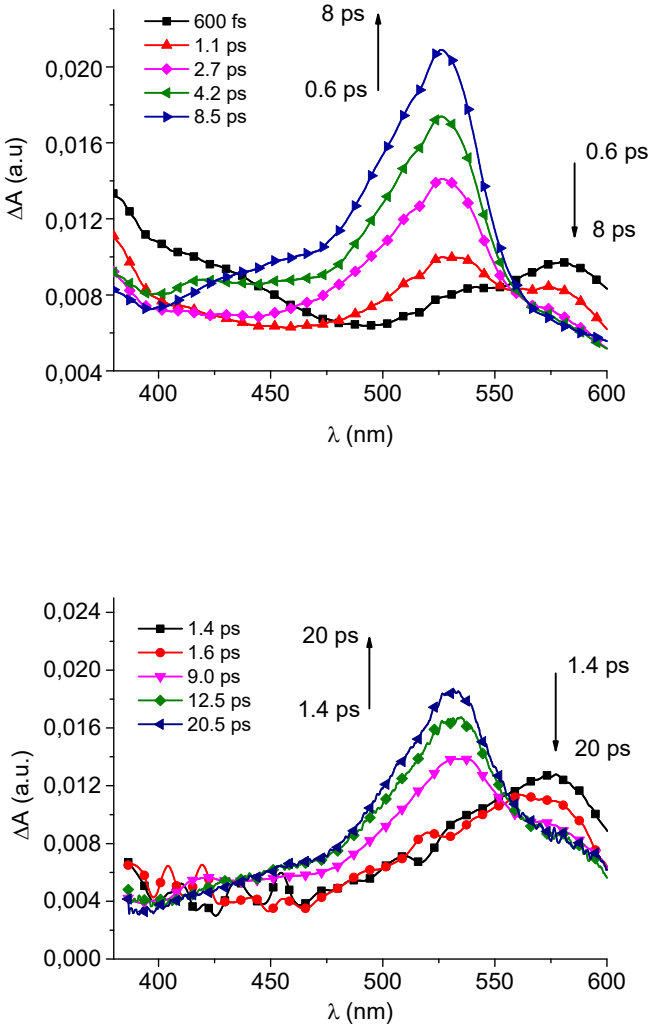

Figure S5. Transient absorption spectra of an KP-Me solution in ethanol (up), or in hexane (bottom) at different times after pump excitation

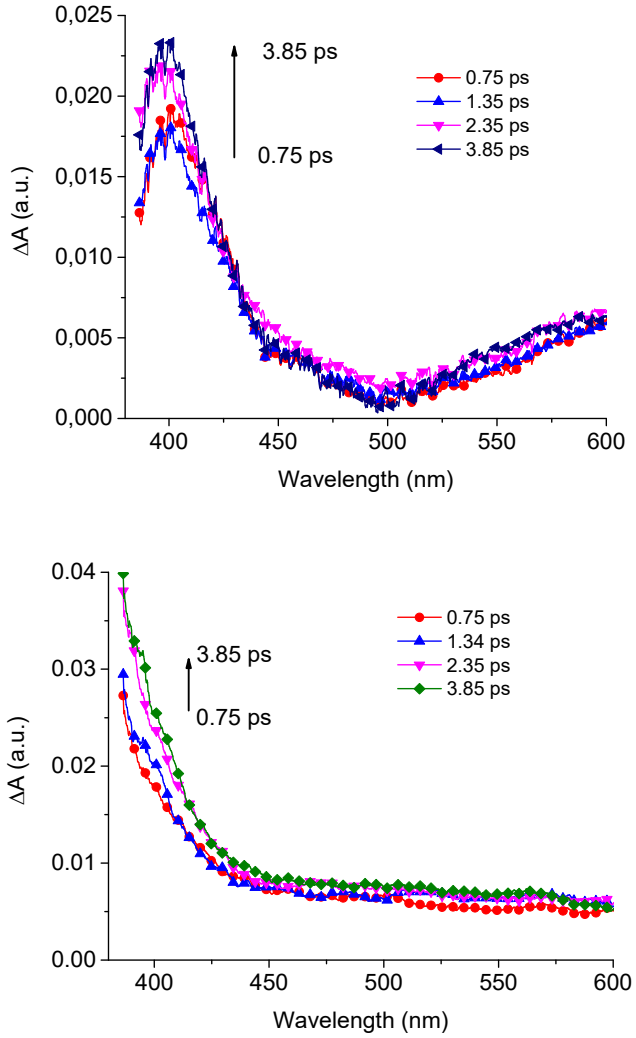

Figure S6. Transient absorption spectra of an AB-Me solution in ethanol (up), or in hexane (bottom) at different times after pump excitation

Table S1. Relative energies (E) in eV of ^{3}AB* and ^{3}KP* states at Franck-Condon (FC) and at the relative equilibrium geometries Q(^{3}AB*) and Q(^{3}KP*), respectively, in n-hexane and ethanol

	FC	Q(^{3}AB*)	Q(^{3}KP*)
		n-Hexane	
E(^{3}AB*)	0.000	-0.322	0.404
E(^{3}KP*)	0.151	0.471	-0.265
		Ethanol	
E(^{3}AB*)	0.000	-0.326	0.320
E(^{3}KP*)	0.084	0.370	-0.350

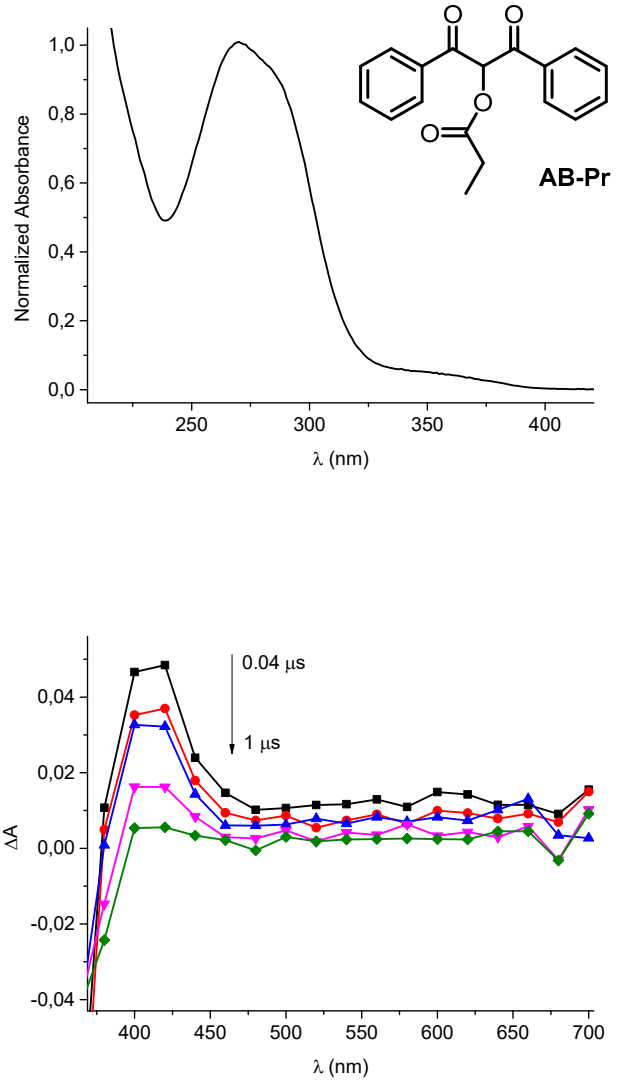

Figure S7. Normalized absorption spectrum in EtOH and structure of AB-Pr (up). Transient absorption spectra of AB-Pr in EtOH under N_2, at different times after the 355 nm laser pulse (bottom)

Table S2. Calculated equilibrium geometries for the dyad

All the coordinates are given in Å, no imaginary frequencies were found.

Franck-Condon region (S0 equilibrium geometry, in vacuo)

E= -1843.10066177 hartree

C	5.542654	-0.897929	-1.804200
C	6.031877	-1.298128	-0.557085
C	4.524095	0.039944	-1.911710
C	3.950923	0.602961	-0.771487
C	4.431294	0.211993	0.483015
C	5.455055	-0.716733	0.580717
C	7.156092	-2.326966	-0.395394
C	7.653409	-2.864998	-1.744214
C	8.345088	-1.666772	0.328971
C	6.640718	-3.516493	0.437610
C	2.870055	1.610339	-0.954624
C	2.074373	2.043734	0.283890
C	1.044445	3.141239	-0.042798
C	-0.307767	2.777988	-0.528608
C	-1.318657	3.744646	-0.423943
C	-2.598646	3.480270	-0.866374
C	-2.893891	2.239397	-1.446873
C	-1.893536	1.274817	-1.581870
C	-0.615194	1.547134	-1.111759
O	-4.179675	2.064313	-1.829681
C	-4.509998	0.895705	-2.551567
O	2.603287	2.082692	-2.040475
O	1.383584	4.291270	0.145094
O	1.480013	0.854208	0.811565
C	1.057142	0.917814	2.090866
C	0.252925	-0.315481	2.456082
C	-1.170090	-0.126857	1.947516
C	0.293511	-0.565419	3.965497
C	-1.899457	1.016936	2.291706
C	-3.204964	1.181393	1.849591
C	-3.810545	0.197634	1.073837
C	-3.089077	-0.940966	0.712360
C	-1.766753	-1.086890	1.140803
C	-3.632478	-1.952589	-0.246078
C	-5.094609	-2.275261	-0.244065
C	-5.657303	-2.768398	-1.425848
C	-7.004097	-3.100878	-1.475265
C	-7.796236	-2.966363	-0.335760
C	-7.238014	-2.499865	0.850935
C	-5.892301	-2.149681	0.897126
O	-2.885522	-2.489446	-1.048831
O	1.268455	1.860173	2.813881
H	5.956929	-1.316496	-2.714210
H	4.156584	0.349764	-2.884742
H	4.017160	0.634019	1.393258
H	5.812077	-0.992658	1.568691
H	6.854682	-3.368477	-2.300071
H	8.449924	-3.597298	-1.575088
H	8.065357	-2.068655	-2.373657
H	8.727085	-0.815580	-0.244500
H	9.158854	-2.390520	0.452718
H	8.066799	-1.304315	1.323658
H	5.784390	-3.993389	-0.051325
H	6.326897	-3.207608	1.439861
H	7.430863	-4.267321	0.552656
H	2.743763	2.486772	1.027793
H	-1.073294	4.706228	0.014931
H	-3.391556	4.215804	-0.781271
H	-2.099542	0.302085	-2.012879
H	0.142048	0.779075	-1.211380
H	-5.567990	0.986877	-2.799278
H	-4.360136	-0.009270	-1.952885
H	-3.921685	0.818062	-3.473923
H	0.695284	-1.163387	1.923766
H	-0.112489	0.291358	4.509030
H	-0.300710	-1.450031	4.211031
H	1.320205	-0.726402	4.307725
H	-1.429842	1.793200	2.889950
H	-3.748186	2.088182	2.094385
H	-4.821750	0.344321	0.706910
H	-1.209961	-1.962316	0.818721
H	-5.018889	-2.885398	-2.295837
H	-7.437897	-3.472664	-2.398485
H	-8.849157	-3.229757	-0.373004
H	-7.849807	-2.409563	1.743197
H	-5.457408	-1.793967	1.825839

Ethanol

T1 E= -1843.00785580 hartree

C	5.279464	-0.951533	-1.854639
C	5.821316	-1.364341	-0.632484
C	4.325656	0.056054	-1.915732
C	3.867811	0.675108	-0.750619
C	4.399828	0.269918	0.479768
C	5.363946	-0.724061	0.529122
C	6.883227	-2.463595	-0.524240
C	7.216013	-3.087364	-1.886458
C	8.173330	-1.857473	0.062055
C	6.369731	-3.580614	0.405175
C	2.859706	1.754999	-0.878819
C	2.096761	2.195996	0.378613
C	1.040299	3.265715	0.047511
C	-0.298201	2.863373	-0.434004
C	-1.332102	3.811717	-0.373263
C	-2.597905	3.510572	-0.830460
C	-2.859861	2.247958	-1.383922
C	-1.836790	1.299459	-1.471633
C	-0.574040	1.607885	-0.984704
O	-4.126699	2.041918	-1.795104
C	-4.444992	0.804549	-2.413814
O	2.622171	2.304591	-1.939130
O	1.354573	4.431084	0.210407
O	1.536672	1.021788	0.965380
C	1.052801	1.162181	2.217018
C	0.312496	-0.083406	2.657524
C	-1.111517	0.009896	2.121545
C	0.349449	-0.237612	4.179689
C	-1.912290	1.111293	2.435647
C	-3.224633	1.183266	1.960903
C	-3.745958	0.178013	1.167785
C	-2.959422	-0.951210	0.855836
C	-1.630210	-1.010139	1.334435
C	-3.443556	-1.989812	-0.030977
C	-4.819006	-2.376626	-0.294371
C	-5.161056	-2.952148	-1.537871
C	-6.471325	-3.334163	-1.794727
C	-7.460725	-3.157095	-0.829529
C	-7.126041	-2.603826	0.411245
C	-5.820056	-2.235376	0.689106
O	-2.524841	-2.616289	-0.713696
O	1.170016	2.182950	2.853927
H	5.599861	-1.415326	-2.780215
H	3.919714	0.368284	-2.872468
H	4.077782	0.732791	1.406481
H	5.766552	-1.005181	1.497302
H	6.335397	-3.548393	-2.347117
H	7.970070	-3.870146	-1.753391
H	7.626400	-2.349238	-2.584178
H	8.558741	-1.062963	-0.586252
H	8.944051	-2.631454	0.150325
H	8.007857	-1.433054	1.057546
H	5.446587	-4.020654	0.012446
H	6.168849	-3.212626	1.416114
H	7.120999	-4.374457	0.483068
H	2.791549	2.669400	1.080118
H	-1.123090	4.789295	0.048507
H	-3.404887	4.233269	-0.772294
H	-2.015591	0.317196	-1.891488
H	0.195909	0.848197	-1.046725
H	-5.505213	0.859053	-2.659326
H	-4.274457	-0.035919	-1.733439
H	-3.862834	0.659713	-3.330514
H	0.802349	-0.939707	2.185366
H	-0.108044	0.625310	4.670491
H	-0.201472	-1.136173	4.469931
H	1.379535	-0.330421	4.536226
H	-1.510371	1.922280	3.035509
H	-3.833180	2.050890	2.195247
H	-4.748263	0.270765	0.762539
H	-1.018963	-1.875788	1.099672
H	-4.399437	-3.065148	-2.302128
H	-6.722430	-3.765544	-2.758921
H	-8.485098	-3.450377	-1.035611
H	-7.890353	-2.475357	1.171621
H	-5.563774	-1.840956	1.667201

T2 E= -1843.00885579 hartree

C	5.485805	-0.979772	-1.841534
C	6.044011	-1.309446	-0.601735
C	4.440925	-0.070218	-1.940902
C	3.908604	0.534194	-0.799396
C	4.459110	0.212981	0.447472
C	5.508777	-0.687473	0.536323
C	7.198152	-2.305180	-0.448316
C	7.642054	-2.895905	-1.793774
C	8.404028	-1.585605	0.185945
C	6.750667	-3.463321	0.464402
C	2.793772	1.504567	-0.969074
C	2.041082	1.978466	0.287116
C	0.950432	3.015628	-0.005144
C	-0.378618	2.602265	-0.391686
C	-1.427152	3.595011	-0.320490
C	-2.704197	3.278023	-0.665295
C	-3.015131	1.961779	-1.137722
C	-1.991636	0.975005	-1.251863
C	-0.708164	1.286307	-0.897721
O	-4.314309	1.758630	-1.431566
C	-4.712926	0.538280	-2.035121
O	2.467535	1.925732	-2.063203
O	1.235916	4.226155	0.096941
O	1.497002	0.803042	0.889931
C	1.099437	0.918282	2.172877
C	0.244437	-0.269036	2.564256
C	-1.135914	-0.047525	1.960679
C	0.200873	-0.452977	4.082981
C	-1.836079	1.141064	2.200671
C	-3.093431	1.345708	1.647648
C	-3.679229	0.359221	0.859561
C	-2.988386	-0.828682	0.608250
C	-1.713630	-1.016234	1.150246
C	-3.507378	-1.859288	-0.343203
C	-4.978271	-2.112167	-0.438157
C	-5.481668	-2.624249	-1.640151
C	-6.837226	-2.893097	-1.773700
C	-7.698637	-2.675177	-0.698093
C	-7.201737	-2.188133	0.508563
C	-5.846434	-1.900975	0.638429
O	-2.726031	-2.470952	-1.058635
O	1.310786	1.895858	2.850784
H	5.864413	-1.432352	-2.750745
H	4.020796	0.179954	-2.909758
H	4.081265	0.666291	1.357888
H	5.918347	-0.908504	1.517349
H	6.829368	-3.442030	-2.285555
H	8.462510	-3.601963	-1.628232
H	8.004495	-2.121919	-2.479207
H	8.738909	-0.755544	-0.445622
H	9.238132	-2.286646	0.302491
H	8.164969	-1.182910	1.175525
H	5.883809	-3.981793	0.040053
H	6.478805	-3.113122	1.465486
H	7.563765	-4.189669	0.574291
H	2.737868	2.464695	0.977223
H	-1.184817	4.590518	0.033262
H	-3.503532	4.007311	-0.588324
H	-2.208858	-0.029194	-1.594975
H	0.050191	0.520165	-0.989907
H	-5.782762	0.629544	-2.219024
H	-4.535912	-0.312482	-1.369872
H	-4.188633	0.376221	-2.982514
H	0.680564	-1.153765	2.091314
H	-0.203576	0.438516	4.569818
H	-0.434633	-1.306430	4.333576
H	1.203409	-0.634457	4.481386
H	-1.380446	1.921321	2.804188
H	-3.612482	2.283705	1.815198
H	-4.651816	0.533861	0.410013
H	-1.173982	-1.928548	0.913461
H	-4.795281	-2.802403	-2.461809
H	-7.224433	-3.277633	-2.712007
H	-8.758284	-2.888124	-0.801117
H	-7.868604	-2.032300	1.350553
H	-5.461998	-1.529938	1.583134

Cyclohexane

T1 E= -1842.99776071 hartree

C	5.436131	-0.892866	-1.834459
C	5.951876	-1.291930	-0.597396
C	4.424752	0.054843	-1.921378
C	3.884892	0.628247	-0.769513
C	4.391426	0.237812	0.475541
C	5.408628	-0.700076	0.552081
C	7.070535	-2.329864	-0.459231
C	7.533638	-2.872896	-1.818150
C	8.280555	-1.678761	0.238281
C	6.562969	-3.513757	0.386651
C	2.816260	1.649505	-0.929563
C	2.030219	2.071582	0.318436
C	0.976300	3.148215	-0.000259
C	-0.359048	2.762492	-0.509481
C	-1.379957	3.724140	-0.460347
C	-2.645430	3.439448	-0.929909
C	-2.918929	2.179181	-1.480095
C	-1.906643	1.219691	-1.561803
C	-0.643210	1.513358	-1.066831
O	-4.190498	1.982848	-1.889112
C	-4.522688	0.739812	-2.480716
O	2.553427	2.151455	-2.004652
O	1.286552	4.305179	0.207786
O	1.456537	0.884089	0.868585
C	1.145998	0.920030	2.182504
C	0.337412	-0.300543	2.577100
C	-1.084127	-0.115301	2.062261
C	0.378312	-0.521525	4.090277
C	-1.792987	1.052096	2.357830
C	-3.101024	1.213106	1.897370
C	-3.711870	0.227904	1.143489
C	-3.022947	-0.969215	0.858310
C	-1.695059	-1.115898	1.318051
C	-3.605730	-1.997038	0.019659
C	-5.011683	-2.277871	-0.205815
C	-5.424204	-2.878980	-1.414667
C	-6.766717	-3.151881	-1.638681
C	-7.721872	-2.838973	-0.674237
C	-7.319328	-2.261314	0.533440
C	-5.981783	-1.999391	0.778812
O	-2.751461	-2.720644	-0.655055
O	1.450498	1.834014	2.909429
H	5.824692	-1.319350	-2.752036
H	4.038790	0.362753	-2.887786
H	4.007409	0.670527	1.393984
H	5.787953	-0.973860	1.532106
H	6.719323	-3.371853	-2.355210
H	8.328542	-3.610365	-1.665019
H	7.937016	-2.080271	-2.457754
H	8.656563	-0.831164	-0.344535
H	9.090470	-2.409645	0.342913
H	8.028252	-1.314587	1.239242
H	5.693400	-3.985048	-0.084141
H	6.273254	-3.200655	1.394860
H	7.350006	-4.269942	0.485692
H	2.706457	2.529396	1.046921
H	-1.156531	4.698910	-0.039432
H	-3.444385	4.171815	-0.883256
H	-2.094757	0.238904	-1.981270
H	0.120470	0.747477	-1.123886
H	-5.585542	0.795904	-2.716009
H	-4.351400	-0.091314	-1.788070
H	-3.952039	0.573137	-3.401957
H	0.778249	-1.160313	2.062050
H	-0.037750	0.340277	4.618201
H	-0.209495	-1.406447	4.349297
H	1.405505	-0.668697	4.436510
H	-1.319202	1.846754	2.927234
H	-3.632839	2.136224	2.104041
H	-4.705319	0.392338	0.739289
H	-1.157658	-2.033694	1.100754
H	-4.687102	-3.101466	-2.178945
H	-7.070270	-3.605214	-2.577555
H	-8.771571	-3.046896	-0.855378
H	-8.057052	-2.028096	1.295241
H	-5.674371	-1.584699	1.733499

T2 E= -1842.99570622 hartree

C	5.571246	-0.938273	-1.829089
C	6.135363	-1.252348	-0.588373
C	4.494602	-0.067492	-1.932764
C	3.931789	0.511320	-0.790672
C	4.490253	0.208654	0.458254
C	5.570403	-0.653745	0.548374
C	7.325577	-2.204851	-0.431570
C	7.799026	-2.773574	-1.776329
C	8.501080	-1.443912	0.211538
C	6.918138	-3.383441	0.473727
C	2.781629	1.434594	-0.960749
C	2.016395	1.883238	0.297204
C	0.920060	2.914317	0.008342
C	-0.396087	2.498041	-0.441699
C	-1.456233	3.461688	-0.373896
C	-2.721571	3.132189	-0.773050
C	-2.990465	1.837107	-1.295528
C	-1.948655	0.883590	-1.409955
C	-0.677284	1.210603	-1.004348
O	-4.278739	1.611132	-1.636757
C	-4.611940	0.403531	-2.295286
O	2.457120	1.861283	-2.059712
O	1.195203	4.120773	0.138080
O	1.473580	0.695799	0.877718
C	1.097730	0.775117	2.171004
C	0.219838	-0.405152	2.536177
C	-1.172545	-0.123011	1.988112
C	0.214046	-0.647161	4.047462
C	-1.828170	1.073086	2.302595
C	-3.097019	1.335884	1.804216
C	-3.738830	0.401112	0.997465
C	-3.092318	-0.792456	0.670187
C	-1.805619	-1.038658	1.157657
C	-3.671942	-1.763621	-0.308640
C	-5.153053	-1.970753	-0.366468
C	-5.706389	-2.418254	-1.571307
C	-7.072377	-2.643372	-1.674085
C	-7.895190	-2.446374	-0.565408
C	-7.348787	-2.024638	0.643772
C	-5.982478	-1.781471	0.743423
O	-2.934884	-2.361690	-1.078108
O	1.349376	1.715287	2.885041
H	5.971067	-1.373474	-2.737799
H	4.070275	0.170107	-2.902888
H	4.091235	0.645654	1.367949
H	5.982893	-0.863292	1.530973
H	7.010083	-3.347856	-2.274613
H	8.644713	-3.449247	-1.610104
H	8.135775	-1.983796	-2.456762
H	8.807321	-0.599089	-0.414567
H	9.361216	-2.112716	0.330844
H	8.242020	-1.053529	1.200940
H	6.073283	-3.931887	0.043149
H	6.627518	-3.048017	1.474541
H	7.756799	-4.080098	0.586239
H	2.704236	2.362225	1.001616
H	-1.244256	4.447433	0.024849
H	-3.538243	3.842087	-0.695453
H	-2.133356	-0.113857	-1.790560
H	0.101088	0.464641	-1.099443
H	-5.678357	0.464640	-2.512288
H	-4.426106	-0.467477	-1.658146
H	-4.051877	0.294164	-3.230878
H	0.617824	-1.281706	2.015808
H	-0.149410	0.236167	4.578757
H	-0.438517	-1.491776	4.285055
H	1.221710	-0.870135	4.410522
H	-1.327075	1.814001	2.919658
H	-3.580637	2.281152	2.027763
H	-4.719750	0.622777	0.588349
H	-1.301749	-1.953469	0.859233
H	-5.047542	-2.584031	-2.417770
H	-7.497883	-2.979374	-2.614612
H	-8.963233	-2.625851	-0.644338
H	-7.985791	-1.886052	1.511726
H	-5.558362	-1.461253	1.689829