

Electronic Supplementary Information

***E–Z* Photoisomerization in Proton-Modulated Photoswitchable Merocyanine Based on Benzothiazolium and o-Hydroxynaphthalene Platform**

Aleksey A. Vasilev ^{1,2,*}, Stanislav Balushev ^{3,4}, Sonia Ilieva ¹, Diana Cheshmedzhieva ^{1,*}

¹ Faculty of Chemistry and Pharmacy, Sofia University “Saint Kliment Ohridski”,
1 James Bourchier Blvd., 1164 Sofia, Bulgaria

² Institute of Polymers, Bulgarian Academy of Sciences, Akad. G. Bonchev St., bl 103A,
1113 Sofia; Bulgaria

³ Faculty of Physics, Sofia University “Saint Kliment Ohridski”, 5 James Bourchier Blvd.,
1164 Sofia, Bulgaria

⁴ Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany

* Correspondence: dvalentinova@chem.uni-sofia.bg; Tel.: +359-2-8161-354

Table of Content

Figure S1. ¹ H-NMR spectrum of dye 3 in DMSO-d ₆ .	S2
Figure S2. ¹ H-NMR spectrum of dye 3 in DMSO-d ₆ – methyl groups region.	S3
Figure S3. ¹ H-NMR spectrum of dye 3 in DMSO-d ₆ – aromatic region.	S4
Figure S4. ¹³ C-NMR DEPT spectrum of dye 3 in DMSO-d ₆ .	S5
Figure S5. ESI-MS (m/z) spectra of dye 3 .	S6
Figure S6. B3LYP/6-31G(d,p) optimized ground state structures with iodine counterion (in water medium) and computed relative Gibbs free energies for the dye 3 isomers.	S7
Cartesian coordinates of the optimized structures from B3LYP/6-31G** calculations in water medium	S8

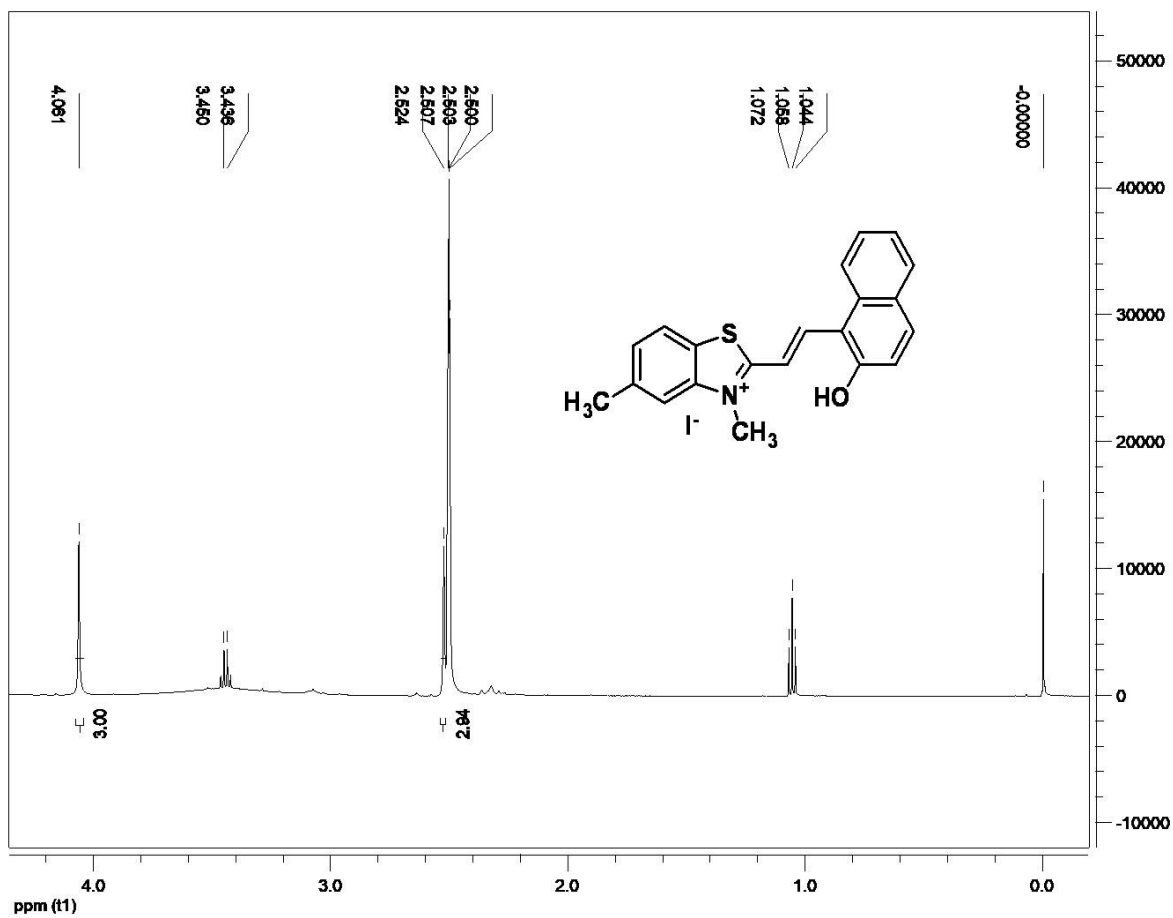


Figure S2. ^1H -NMR spectrum of dye 3 in DMSO-d_6 – methyl groups region.

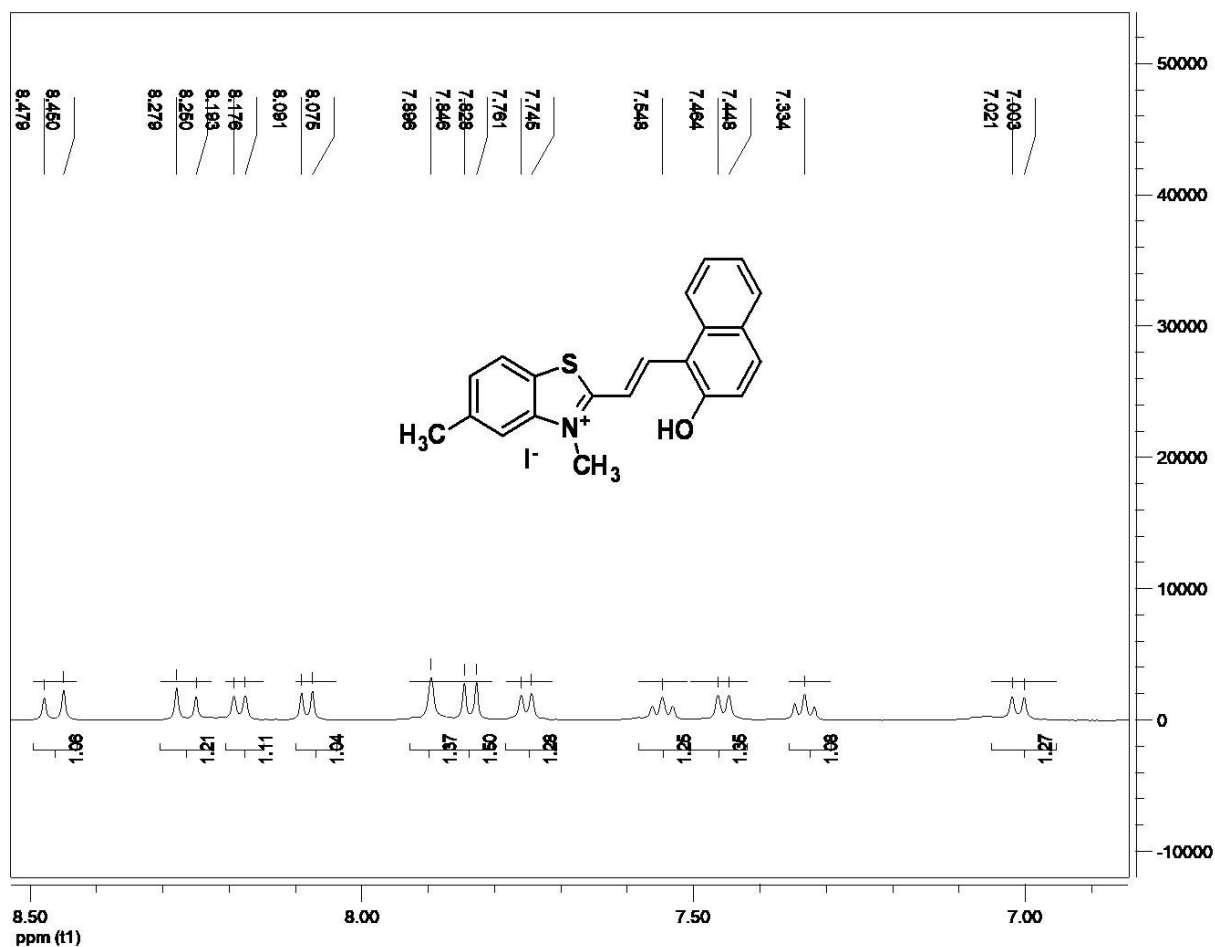


Figure S3. ¹H-NMR spectrum of dye 3 in DMSO-d₆ – aromatic region.

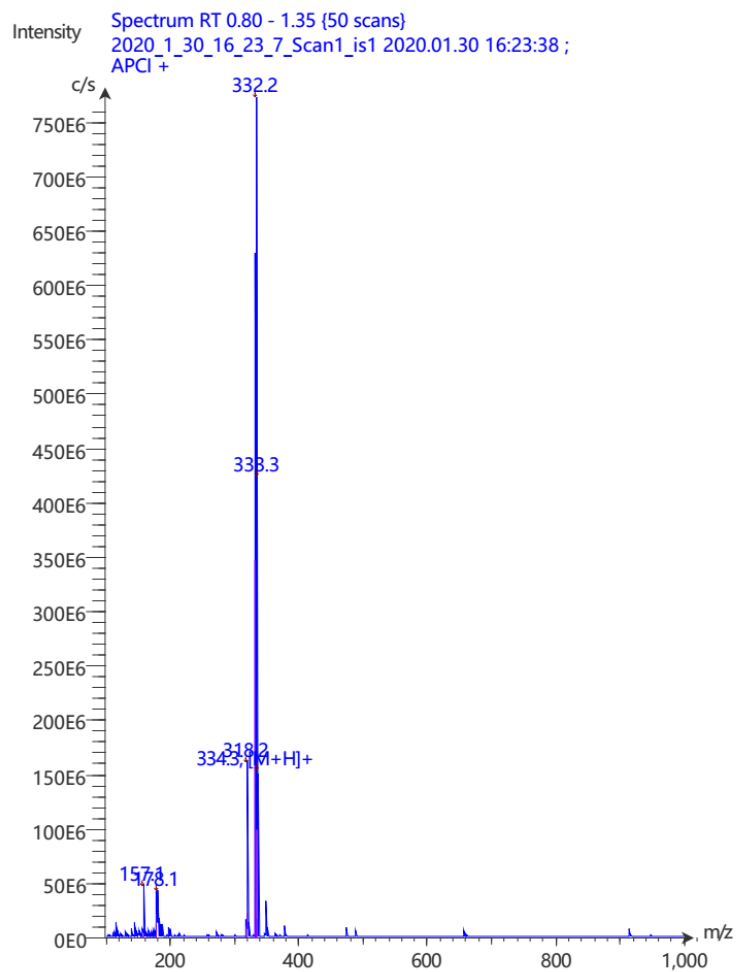


Figure S5. ESI-MS (m/z) spectra of dye **3**.

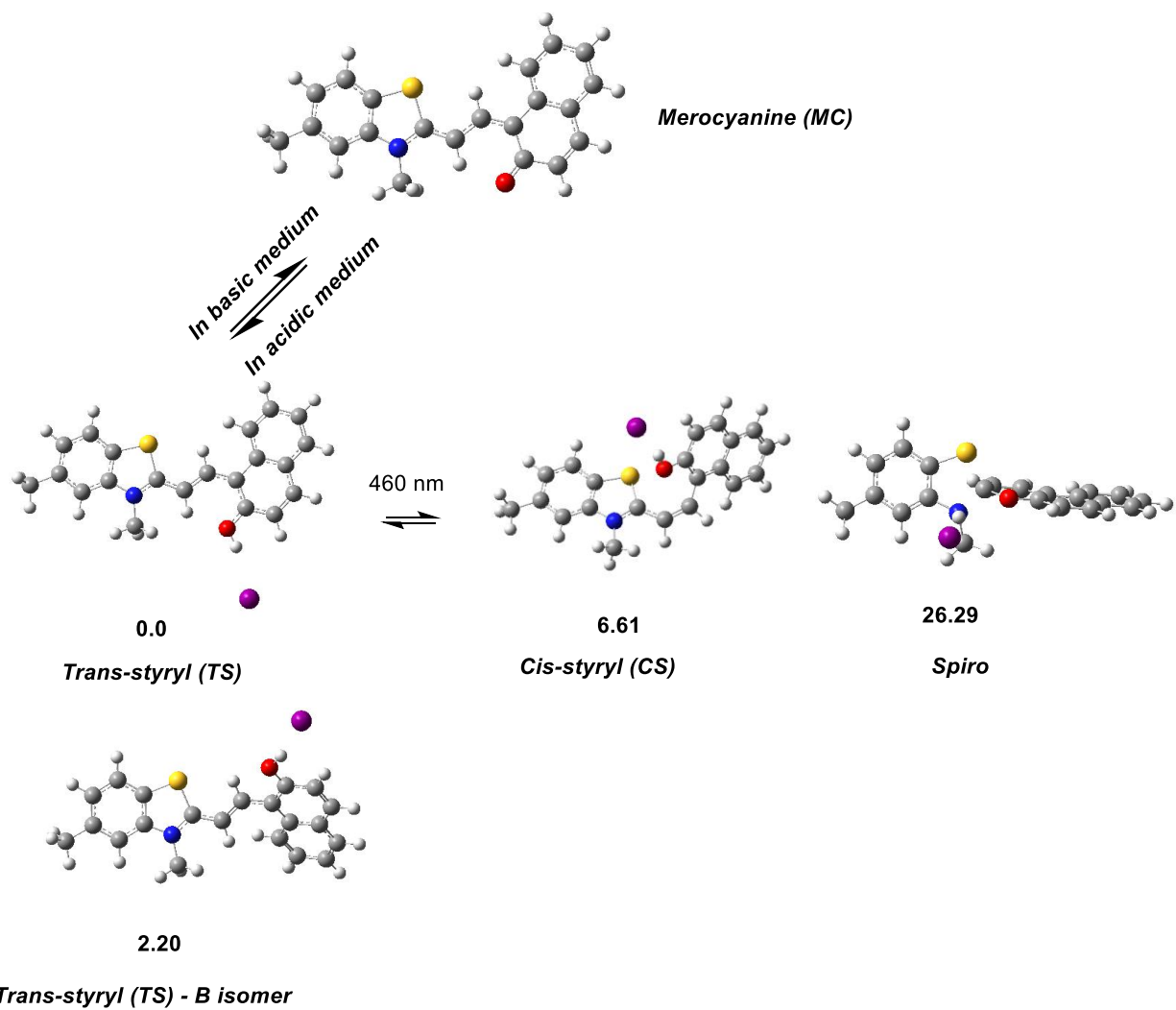


Figure S6. B3LYP/6-31G(d,p) optimized ground state structures with iodine counterion (in water medium) and computed relative Gibbs free energies for the dye **3** isomers.

Cartesian coordinates of the optimized structures from B3LYP/6-31G** calculations in water medium

Trans (TS)

C, 0, -5.5083079723, -2.0007959053, 0.0385449342
C, 0, -5.8982094496, -0.6496363994, 0.1625284405
C, 0, -4.9205035633, 0.3442524036, 0.2118654476
C, 0, -3.5721495651, -0.0246416556, 0.1398252262
C, 0, -3.2064830881, -1.371182657, 0.0068652066
C, 0, -4.17311798, -2.3759809614, -0.0419422917
N, 0, -2.4549832692, 0.8226533873, 0.1830948052
C, 0, -1.2657242727, 0.1978215376, 0.0572096129
S, 0, -1.4627119157, -1.5308585805, -0.0951210679
C, 0, -7.3626241149, -0.2927493666, 0.2372252241
C, 0, -2.5851997681, 2.2784990842, 0.3478440488
C, 0, -0.0106567177, 0.8724703781, 0.0291736896
C, 0, 1.1839205149, 0.2008690454, 0.0120679244
C, 0, 2.529527028, 0.7050622823, -0.0351202081
C, 0, 2.823338149, 2.0829865794, -0.1286836066
C, 0, 4.1516210876, 2.5589081967, -0.1960448971
C, 0, 5.2024242557, 1.6799312623, -0.1701971175
C, 0, 4.9904867649, 0.2787147061, -0.0710994997
C, 0, 3.651507021, -0.2267484503, 0.0021119645
C, 0, 6.096630954, -0.6090109207, -0.0420300281
C, 0, 5.9095033484, -1.9690907929, 0.0595067126
C, 0, 4.5963852642, -2.4772738769, 0.1387102417
C, 0, 3.5020445247, -1.6340841482, 0.1126081964
O, 0, 1.8004706837, 2.9652278828, -0.1599363582
H, 0, -6.2742985767, -2.7693104565, 0.000867423
H, 0, -5.2134065435, 1.3839902072, 0.2950675552
H, 0, -3.8907046991, -3.417732545, -0.1422687468
H, 0, -7.8377967155, -0.7723603561, 1.0996460255
H, 0, -7.5086909149, 0.7860187891, 0.3256578156
H, 0, -7.8950225141, -0.636826017, -0.6558702972
H, 0, -1.7631058281, 2.6539629318, 0.9532957751
H, 0, -2.5904393941, 2.7701037488, -0.6273303818
H, 0, -3.5151332305, 2.4878540663, 0.8709411882
H, 0, -0.032756608, 1.9499669284, 0.0115513291
H, 0, 1.1141787825, -0.8810123436, 0.0403144119
H, 0, 4.3251099533, 3.6284387654, -0.2706487114
H, 0, 6.2205435162, 2.0535112842, -0.2242917305
H, 0, 7.0969301412, -0.1896229325, -0.1010803666
H, 0, 6.7586718052, -2.6442772592, 0.0811276718
H, 0, 4.437962711, -3.5479745457, 0.2235953565
H, 0, 2.5205238788, -2.0854553198, 0.1848020065
H, 0, 2.1390763167, 3.869778023, -0.2357239244

Trans B

C, 0, -6.3695296847, -2.4617470267, 0.5652161525
C, 0, -6.8769066056, -1.4188797685, -0.2404078885
C, 0, -6.0285792835, -0.3847416092, -0.6363482524
C, 0, -4.6915727453, -0.4099394625, -0.2239963077
C, 0, -4.2087985795, -1.4485826574, 0.5833056389
C, 0, -5.0454464027, -2.4905455198, 0.9849260604
N, 0, -3.6956973649, 0.5287314958, -0.530042085
C, 0, -2.4936507151, 0.2743096299, 0.0239010097
S, 0, -2.5196036637, -1.1867315984, 0.9768723649
C, 0, -8.3258235645, -1.4299190298, -0.661882737
C, 0, -3.972902928, 1.6787420546, -1.4034295628
C, 0, -1.340656269, 1.1044670783, -0.110795792
C, 0, -0.0849938724, 0.684596139, 0.2316321171
C, 0, 1.1611457273, 1.4055098132, 0.1601106723
C, 0, 2.3225187122, 0.6172649905, 0.0147901991
C, 0, 3.5961873383, 1.1982043453, -0.180865186
C, 0, 3.7251314378, 2.562331614, -0.2218211899

C, 0, 2.6079302517, 3.4188815028, -0.0203119243
C, 0, 1.3123901618, 2.8472032403, 0.2052295831
C, 0, 2.77789958, 4.8264886843, -0.0038596417
C, 0, 1.7173425533, 5.6650858754, 0.2625126217
C, 0, 0.4550095246, 5.1081503405, 0.5523144238
C, 0, 0.2581046171, 3.739751639, 0.5285869834
O, 0, 2.1787221321, -0.7285700504, 0.0097404804
H, 0, -7.0351082705, -3.263749421, 0.8694762104
H, 0, -6.4094125065, 0.4249836653, -1.2471945992
H, 0, -4.674490186, -3.2964647262, 1.6078229363
H, 0, -8.5583558871, -2.3327386968, -1.236655478
H, 0, -8.9868465018, -1.4253662937, 0.2113379294
H, 0, -8.5708090676, -0.5621909021, -1.2782700519
H, 0, -4.4243057476, 2.4883885243, -0.8261361314
H, 0, -3.0528818069, 2.0193978065, -1.870387461
H, 0, -4.6553405103, 1.3597134446, -2.1898097139
H, 0, -1.4957827325, 2.0840583864, -0.5404475808
H, 0, 0.0265472332, -0.3554638638, 0.5295509475
H, 0, 4.4591523316, 0.554012218, -0.3212160115
H, 0, 4.7003761323, 3.0073971292, -0.395408751
H, 0, 3.7688548601, 5.2302998637, -0.1908250809
H, 0, 1.8551212335, 6.741362807, 0.2757746371
H, 0, -0.3742922197, 5.7593860706, 0.811077216
H, 0, -0.7126734707, 3.3534656843, 0.8074199024
H, 0, 3.0445597589, -1.1576244167, -0.0506626594

Cis (CS)

C, 0, -4.7039589854, -1.078268985, -1.5471468258
C, 0, -5.3290966817, -0.2730630175, -0.5676468594
C, 0, -4.5488538821, 0.3553945513, 0.401462138
C, 0, -3.1617310115, 0.1683158497, 0.376060173
C, 0, -2.5594405575, -0.6405182144, -0.5971619604
C, 0, -3.3296933659, -1.2714089236, -1.5768896945
N, 0, -2.2192850767, 0.7221774809, 1.2519192224
C, 0, -0.9475399816, 0.359017305, 1.0126820065
S, 0, -0.8258030119, -0.6930420908, -0.3625944671
C, 0, -6.8284851179, -0.1056231295, -0.578462402
C, 0, -2.6225633386, 1.6409938238, 2.3278127242
C, 0, 0.1471768603, 0.6833419715, 1.8885478914
C, 0, 1.4805386211, 0.6635701976, 1.6249291892
C, 0, 2.2279204166, 0.5721508651, 0.3754624868
C, 0, 1.8759801501, 1.3157372173, -0.759128469
C, 0, 2.7102110612, 1.3468370699, -1.9038815858
C, 0, 3.8904381975, 0.6495488966, -1.9235634816
C, 0, 4.3065322015, -0.1225477617, -0.8050854262
C, 0, 3.4716161012, -0.1647479718, 0.3568520284
C, 0, 5.5248951249, -0.8488142078, -0.8259527981
C, 0, 5.918519906, -1.5995823602, 0.2603706024
C, 0, 5.0915804113, -1.6572699055, 1.4037224173
C, 0, 3.8956222186, -0.9679896763, 1.4480864542
O, 0, 0.7330936075, 2.0443155477, -0.7344010687
H, 0, -5.3190244778, -1.5626364453, -2.2993769384
H, 0, -5.0158476895, 0.9686508856, 1.1630916616
H, 0, -2.8689658018, -1.8947263014, -2.3347132911
H, 0, -7.3297301281, -1.0706021062, -0.4468405898
H, 0, -7.1632547907, 0.5625277589, 0.2178999528
H, 0, -7.1683915224, 0.3055629075, -1.5348277378
H, 0, -3.010923032, 1.0742907197, 3.1766018287
H, 0, -1.7698645233, 2.2407856146, 2.6336352941
H, 0, -3.3942144424, 2.3061777217, 1.942210246
H, 0, -0.1407985961, 0.8789205585, 2.9161137689
H, 0, 2.1054710396, 0.7597850957, 2.5104895319
H, 0, 2.4043355981, 1.9408909688, -2.760400534
H, 0, 4.5241602834, 0.6834938061, -2.8047708337

H,0,6.1416325603,-0.8025196493,-1.7191931156
H,0,6.8523906837,-2.1520439331,0.2374347547
H,0,5.3928877065,-2.260262224,2.254929142
H,0,3.2654155589,-1.0631737367,2.3253991364
H,0,0.6458777069,2.5507498268,-1.5550155718

Spiro

C,0,-5.1064659555,-0.6843477468,0.7497348751
C,0,-4.7733456948,-1.1812176132,-0.5203817455
C,0,-3.5789648336,-0.7487583659,-1.1152978801
C,0,-2.7797851659,0.1552176229,-0.4314565914
C,0,-3.1051274496,0.6377417307,0.8330397401
C,0,-4.2870745499,0.2126319633,1.4365225056
N,0,-1.5324193198,0.7167416287,-0.9721515175
C,0,-0.6114558341,1.1549867446,0.3144092215
S,0,-1.8938057779,1.7475990785,1.5056364906
C,0,-5.6863068874,-2.1436333706,-1.2396461626
C,0,-1.7836793197,1.8225154157,-1.9600998201
C,0,0.386329242,2.1872606309,-0.0324362628
C,0,1.6884913781,1.8577577531,-0.1578593489
C,0,2.1590598943,0.5088926993,0.0626293001
C,0,1.2292906331,-0.4074572199,0.5334371876
C,0,1.5535150459,-1.7379609179,0.8575400629
C,0,2.8499167344,-2.1586854883,0.6847994096
C,0,3.8567200304,-1.2816246101,0.1916794759
C,0,3.5181798447,0.0745598837,-0.1272527202
C,0,5.1923160037,-1.7280854544,0.011197565
C,0,6.162906359,-0.875689568,-0.4657703815
C,0,5.8297978688,0.4607415889,-0.7834348592
C,0,4.5409041502,0.9251340331,-0.620575534
O,0,-0.0892894995,-0.0506746619,0.7594565844
H,0,-6.0245961795,-1.0196569738,1.222810358
H,0,-3.2878604601,-1.1181452661,-2.093817205
H,0,-4.5606155381,0.5612567217,2.4261781607
H,0,-6.4756465312,-1.60353881,-1.775795372
H,0,-5.1393409361,-2.7408866693,-1.9733492096
H,0,-6.1762187003,-2.8235969213,-0.5374718083
H,0,-2.3346891787,2.6163805859,-1.4580680021
H,0,-0.8260911164,2.1846709452,-2.3299444531
H,0,-2.3747778197,1.4117359565,-2.776922312
H,0,0.0400700983,3.2045815545,-0.1588140752
H,0,2.3973108925,2.639922591,-0.4034906121
H,0,0.7782757981,-2.3971313148,1.2307056332
H,0,3.1204821035,-3.1827184543,0.9236164367
H,0,5.4337445702,-2.7581907865,0.2571490289
H,0,7.1814495038,-1.2254894357,-0.6003931739
H,0,6.5962672972,1.129765192,-1.1622254456
H,0,4.3157676114,1.9530466571,-0.8809545327
H,0,-0.9888193119,-0.0166523286,-1.4384620104

Transition state TS cis-spiro

C,0,-4.6845016812,-1.6699624383,2.1591363567
C,0,-5.0613391942,-1.134266656,0.9175092253
C,0,-4.1182326094,-0.4032239079,0.1818648893
C,0,-2.8429754275,-0.2104551372,0.703366562
C,0,-2.4866194425,-0.7417991798,1.9425098241
C,0,-3.4032108516,-1.4867930487,2.6793079161
N,0,-1.7730374512,0.4728432849,0.0121513779
C,0,-0.4939403073,0.3827503899,0.7900865469
S,0,-0.8215245613,-0.3299210912,2.4111956798
C,0,-6.4617516527,-1.3269778978,0.3875701643
C,0,-2.1104258087,1.7765998349,-0.6200437717
C,0,0.4253961365,1.5416811456,0.8006634032
C,0,1.6111549319,1.546453987,0.1648265275
C,0,2.1287355148,0.4318824468,-0.6145832966
C,0,1.3329139516,-0.685755576,-0.7877074011
C,0,1.7061588779,-1.830809301,-1.5034818055

C,0,2.94928024,-1.8427738579,-2.0939912944
C,0,3.8366855491,-0.740545963,-1.9664909208
C,0,3.4371231009,0.4158724118,-1.2137331478
C,0,5.1216014831,-0.7683723253,-2.5724803903
C,0,5.9844603303,0.2954338739,-2.4453266477
C,0,5.5939168123,1.4337426997,-1.7022946619
C,0,4.354940283,1.4938686545,-1.1012363022
O,0,0.0414603905,-0.7039607043,-0.2146539565
H,0,-5.4066211587,-2.2446135425,2.7312845759
H,0,-4.3834758708,-0.0038603682,-0.7910802878
H,0,-3.1311479944,-1.9104401225,3.6397014982
H,0,-7.141911744,-0.5726876352,0.8009400946
H,0,-6.4936996539,-1.2364015294,-0.7011803773
H,0,-6.8582658683,-2.3079968321,0.6633324506
H,0,-2.4605421221,2.4909323869,0.1275638678
H,0,-1.2293058817,2.161456224,-1.1315942574
H,0,-2.8927371726,1.597435952,-1.3555250429
H,0,0.1052173587,2.3844543578,1.4023516881
H,0,2.2202789756,2.4367690825,0.2597937359
H,0,1.0211975761,-2.6668133478,-1.1582682507
H,0,3.2681874757,-2.7103791296,-2.6628456766
H,0,5.4092356159,-1.649470063,-3.1384993412
H,0,6.9638533372,0.2651490589,-2.9118002311
H,0,6.2782058671,2.2704476947,-1.6029410907
H,0,4.0901672504,2.3804857813,-0.5374864206
H,0,-0.9438508445,-0.4091726024,-0.7377772812

Transition state TS trans- cis

C,0,-5.0464938689,1.7369966584,-0.2724449912
C,0,-5.5883980601,0.4458591312,-0.2471645314
C,0,-4.7330571838,-0.6594372308,-0.1074876344
C,0,-3.3557219281,-0.4638741005,0.0058424992
C,0,-2.8344679091,0.8430103894,-0.0310333312
C,0,-3.6663980236,1.9444680391,-0.1665598373
N,0,-2.3693523148,-1.4395520261,0.1635403741
C,0,-1.0659853498,-0.9587080056,0.1989637563
S,0,-1.0668112224,0.825940408,0.1245473347
C,0,-7.0773876345,0.2265205149,-0.3834458709
C,0,-2.6201273305,-2.8701311201,0.2388329538
C,0,0.0558855924,-1.7077536253,0.2844695521
C,0,1.4124578256,-1.1498709819,0.236488366
C,0,2.2617187304,-0.8101816543,1.259874209
C,0,1.9059285682,-1.0335786823,2.6586750133
C,0,2.853932516,-0.8737203972,3.6824718288
C,0,4.1271445535,-0.4530186702,3.3792219685
C,0,4.5442020805,-0.1422905322,2.0534979901
C,0,3.6205268918,-0.2870574201,0.9777845974
C,0,5.8558175734,0.3285536902,1.8206795534
C,0,6.259557561,0.6693213465,0.5424951403
C,0,5.3474527491,0.5511632844,-0.5156434321
C,0,4.0518216487,0.0872002792,-0.3034209424
O,0,0.6762815383,-1.4182140122,2.9334700664
H,0,-5.7053432605,2.5933423122,-0.3787568403
H,0,-5.154827637,-1.6587815974,-0.0944422091
H,0,-3.2569441237,2.9491496036,-0.1900196881
H,0,-7.3202936573,-0.2654563332,-1.332603407
H,0,-7.4611424622,-0.4151934112,0.4168167008
H,0,-7.6227748465,1.1729045352,-0.3498386547
H,0,-2.2639809604,-3.381005983,-0.6628235929
H,0,-2.1092752724,-3.2917709457,1.1098128601
H,0,-3.6868811268,-3.0516115122,0.3491840444
H,0,-0.0101888088,-2.7926497262,0.2945151854
H,0,1.8265941257,-1.037687376,-0.7662212194
H,0,2.5697817191,-1.0790120418,4.7090191557
H,0,4.8453999244,-0.3344970415,4.185199019
H,0,6.5358804984,0.4226502311,2.661370182
H,0,7.2650511784,1.032289426,0.3605860619
H,0,5.6477880798,0.8309568573,-1.5201137668
H,0,3.3831037552,0.0394839086,-1.1537412789
H,0,0.5623044212,-1.5727913283,3.8874588251

Mero

C,0,5.8328121009,-0.9131390015,0.0389638698
C,0,5.8034004291,0.4873382626,0.1739592316
C,0,4.5717278853,1.1482840504,0.2128311123
C,0,3.3882068012,0.4087680074,0.1140529919
C,0,3.4417642163,-0.9865291926,-0.0203976664
C,0,4.6605283415,-1.6588815805,-0.0590746446
N,0,2.0733924743,0.8917582805,0.1331384171
C,0,1.0998770555,-0.0626161975,0.0241448803
S,0,1.8198984779,-1.6712775259,-0.1197638436
C,0,7.0936431965,1.2671227573,0.2672857401
C,0,1.7242373255,2.3070827346,0.2617655778
C,0,-0.2660760953,0.2080846418,0.0282638486
C,0,-1.2414651689,-0.7907561002,-0.0853423125
C,0,-2.6348262575,-0.6597049535,-0.1058623143
C,0,-3.4888648061,-1.8511571897,-0.2213955689
C,0,-4.9072071185,-1.7010574003,-0.287296785
C,0,-5.4834195863,-0.3813669175,-0.2279145672
C,0,-4.7194240429,0.7294312905,-0.1040371221
C,0,-3.2619372723,0.6722159935,-0.0276616932
C,0,-2.9881362854,-3.1745874253,-0.268502526
C,0,-3.8275365461,-4.2736958439,-0.3838529333
C,0,-5.2197011931,-4.1104162318,-0.4552681398
C,0,-5.7442493635,-2.8297441383,-0.4044472986
O,0,-2.6161973594,1.7409665618,0.0927643595
H,0,6.7900233359,-1.4251458769,0.0113678841
H,0,4.550205778,2.2264651723,0.320243988
H,0,4.6958035023,-2.7381200266,-0.1616013368
H,0,7.7377189613,0.8709255226,1.0592209098
H,0,7.6597301341,1.2031251047,-0.6689222671
H,0,6.9096002654,2.32371818,0.4759076083
H,0,2.6316882553,2.9024186744,0.3064901757
H,0,1.1349193303,2.6267322238,-0.6008374113
H,0,1.146851722,2.4709815572,1.1749465649
H,0,-0.597017651,1.23172149,0.1241713611
H,0,-0.8586825848,-1.8045280938,-0.1758878758
H,0,-6.5669105988,-0.2984087818,-0.2818761972
H,0,-5.1602848002,1.7207752122,-0.0551912864
H,0,-1.9222985474,-3.3619227234,-0.2086741965
H,0,-3.3958950131,-5.2699944172,-0.4161869653
H,0,-5.8725587069,-4.9729332252,-0.5452342859
H,0,-6.8191280811,-2.6744762241,-0.453177093