Supporting Information: Photoswitching of Salicylidene Methylamine: a Theoretical Photodynamics Study

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OM2/MRCI Active Space

The active space in the MRCI calculations included 10 electrons in 10 orbitals. Figure 1 shows the active orbitals for the most stable ground-state conformer of salicylidene methylamine (α isomer).

In the closed-shell wavefunction of the planar ground state, the set of active orbitals consists of the 5 highest occupied orbitals and the 5 lowest unoccupied orbitals. This includes orbitals of π and σ type, so that different types of excitations can be taken into account.

Ab Initio Relative Energies

Ab initio results from previous work are shown here for comparison.[1] Structures were optimized with MP2/cc-pVDZ for ground states and CC2/cc-pVDZ for excited states. Conical intersections were optimized with the CASSCF(6,6)/cc-pVDZ method. Vertical excitations were computed using CC2/aug-cc-pVTZ.

Table 1: Ab Initio Values for Relative Energies, Vertical Excitation Energies, and Important Geometrical Parameters for the Relevant Isomers and Conical Intersections of SMA

	S_0 (kcal/mol)	S_1 (kcal/mol)	Vert. Exc. (eV)	OH (Å)	NH (Å)	CC (°)	CN (°)
α (S_0)	0.0	94.8	4.1	0.997	1.719	0.0	180.0
β (S_0)	Relaxation to α (S_0)						
γ (S_0)	22.1	68.5	2.9	4.743	1.016	179.6	177.9
δ (S_0)	13.8	105.5	4.6	0.971	2.474	-57.0	-4.7
α (S_1)	Relaxation to β (S_1)						
β (S_1)	34.7	65.1	1.7	1.870	1.028	0.0	-150.7
γ (S_1)	50.5	64.6	1.1	4.669	1.021	180.0	168.2
δ (S_1)	Relaxation to CI2						
CI1	–	–	0.0	3.127	1.025	87.7	-168.5
CI2	–	–	0.0	0.948	2.091	-3.5	-90.3

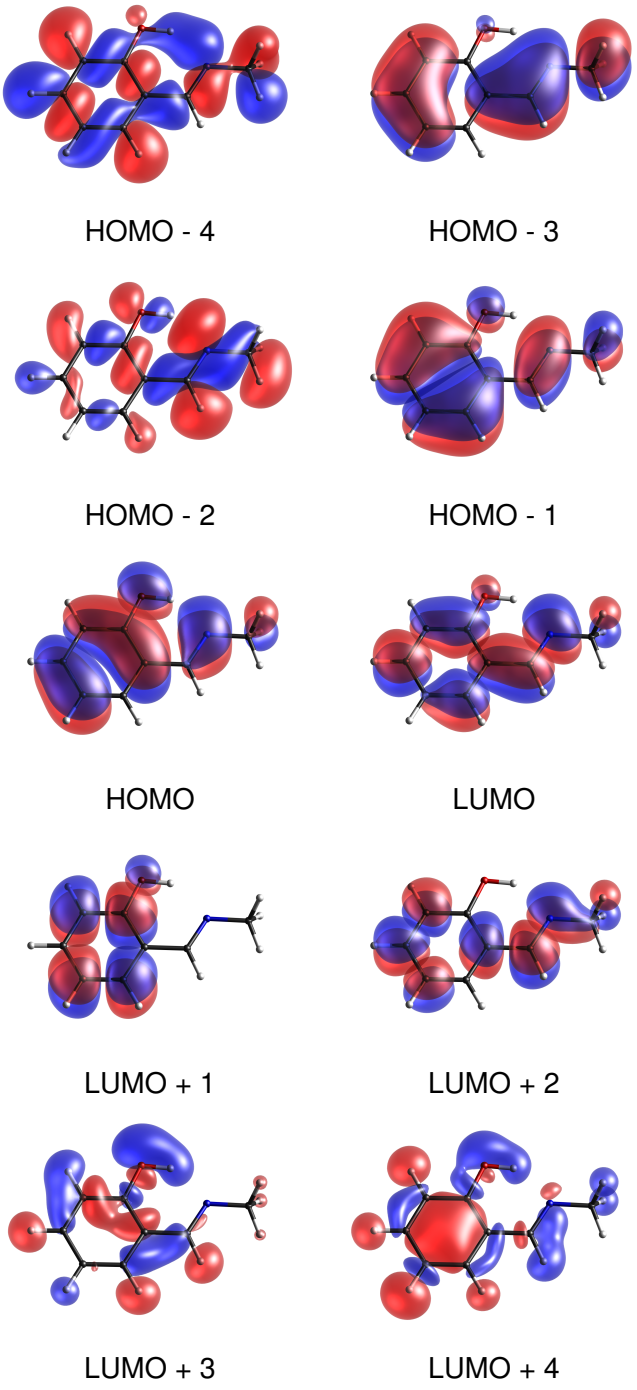

Figure 1: The active space (10e,10o) of salicylidene methylamine (cis-enol form) used in the OM2/MRCI calculations. Orbitals HOMO-3, HOMO-1, HOMO, LUMO, LUMO+1, LUMO+2 are of π type. See text for simulation details.

SMA Photochemical Classes Definition

	OH (Å)	|CC| dihedral angle (°)	|CN| dihedral angle (°)
α	< NH	any value	> 90
β	> NH	< 90	any value
γ	> NH	> 90	any value
δ	< NH	any value	< 90

Cartesian Coordinates of OM2/MRCI Structures

α (S_0)

C	0.92097	2.31494	-0.13836
C	0.89641	0.90692	-0.09367
C	-0.33415	0.21146	0.01820
C	-1.52939	0.94998	0.08380
C	-1.50079	2.33418	0.03954
C	-0.27794	3.01029	-0.07117
O	2.09871	0.30485	-0.16395
C	-0.39552	-1.24771	0.06715
N	0.68064	-1.95480	0.00935
C	0.56090	-3.38289	0.06165
H	-2.48640	0.41847	0.17052
H	-2.42951	2.90434	0.09062
H	-0.27340	4.10590	-0.10487
H	1.87873	2.82565	-0.22450
H	-1.42159	-1.69858	0.15651
H	1.99351	-0.69037	-0.12590
H	1.12462	-3.76280	0.93332
H	-0.49829	-3.73249	0.15039
H	0.99247	-3.81734	-0.85864

β (S_0)

C	0.94021	2.28022	-0.13872
C	0.91848	0.83404	-0.09309
C	-0.38320	0.18258	0.02269
C	-1.57209	0.97208	0.08628
C	-1.49257	2.34277	0.03868
C	-0.22682	2.99247	-0.07440
O	1.96989	0.14557	-0.14962
C	-0.44392	-1.21643	0.06976
N	0.65655	-1.95905	0.01126
C	0.63165	-3.39702	0.05686
H	-2.54714	0.46903	0.17346
H	-2.39708	2.95541	0.08669
H	-0.21165	4.09012	-0.10894
H	1.91366	2.76272	-0.22516
H	-1.43417	-1.72024	0.15808
H	1.56950	-1.45244	-0.07145
H	1.20809	-3.76544	0.93087
H	-0.41101	-3.77122	0.14514
H	1.07542	-3.82020	-0.86828

γ (S_0)

C	0.93227	2.32731	-0.13957
C	0.90580	0.87329	-0.09334
C	-0.40384	0.22091	0.02305
C	-1.59071	1.02437	0.08606
C	-1.50102	2.39162	0.03781
C	-0.22940	3.04039	-0.07567
O	1.94399	0.18518	-0.14890
C	-0.37591	-1.17076	0.06337
N	-1.46461	-1.95469	0.16747
C	-1.38902	-3.39459	0.20576
H	-2.57611	0.53997	0.17343
H	-2.39998	3.01401	0.08511
H	-0.22060	4.13680	-0.10971
H	1.90925	2.80766	-0.22620
H	0.61879	-1.65251	0.00473
H	-2.38559	-1.53643	0.22262
H	-1.94887	-3.83826	-0.64618
H	-0.33408	-3.72793	0.13813
H	-1.81601	-3.78338	1.15581

δ (S_0)

C	0.95739	2.32813	-0.34319
C	0.93745	0.94042	-0.53229
C	-0.20036	0.16373	-0.23050
C	-1.35048	0.80865	0.23610
C	-1.33310	2.18490	0.45054
C	-0.18411	2.93679	0.17447
O	2.09082	0.38424	-1.00844
C	-0.16691	-1.31168	-0.41551
N	0.63916	-2.10265	0.18701
C	1.60022	-1.59060	1.12810
H	-2.25177	0.22280	0.44363
H	-2.22358	2.68132	0.84643
H	-0.18278	4.01766	0.35395
H	1.85468	2.89455	-0.58256
H	-0.91362	-1.70776	-1.13532
H	1.86882	-0.43311	-1.53098
H	2.57164	-1.47252	0.62151
H	1.31352	-0.61803	1.57616
H	1.71197	-2.32710	1.94528

β (S_1)

C	0.94697	2.28388	-0.13936
C	0.91814	0.85977	-0.09382
C	-0.39373	0.19624	0.02308
C	-1.54083	0.95387	0.08453
C	-1.46994	2.39013	0.03557
C	-0.25078	3.02842	-0.07374
O	1.97261	0.16282	-0.15031
C	-0.47444	-1.25706	0.07321
N	0.63877	-1.98023	0.01317
C	0.64146	-3.41957	0.05682
H	-2.53131	0.48346	0.17181
H	-2.39991	2.95915	0.08679
H	-0.20564	4.12168	-0.11035
H	1.90974	2.78397	-0.22550
H	-1.46328	-1.74391	0.16104
H	1.54358	-1.47591	-0.06885
H	1.22374	-3.77638	0.93171
H	-0.39217	-3.81413	0.14506
H	1.09083	-3.83127	-0.87074

γ (S_1)

C	0.93862	2.31488	-0.13966
C	0.89747	0.89832	-0.09349
C	-0.41898	0.25281	0.02319
C	-1.56810	1.00372	0.08502
C	-1.48588	2.44304	0.03513
C	-0.26316	3.06294	-0.07387
O	1.90879	0.13857	-0.14489
C	-0.35884	-1.20863	0.06327
N	-1.44343	-1.96741	0.16630
C	-1.39441	-3.41257	0.20670
H	-2.57339	0.55043	0.17292
H	-2.40908	3.01867	0.08564
H	-0.20973	4.15662	-0.11111
H	1.89999	2.82083	-0.22592
H	0.64716	-1.64035	0.00227
H	-2.36369	-1.53616	0.22099
H	-1.95778	-3.84302	-0.64635
H	-0.34645	-3.76167	0.14007
H	-1.82478	-3.78807	1.15757

S_1S_0 CI1

C	0.97972	2.23940	-0.08427
C	0.85701	0.76862	-0.04914
C	-0.49441	0.18474	0.01641
C	-1.58982	1.02908	0.03072
C	-1.42495	2.41990	-0.00761
C	-0.15535	3.01651	-0.07857
O	1.88666	0.08570	-0.07444
C	-0.74163	-1.27530	0.03582
N	-0.70641	-1.92292	1.24824
C	-0.37435	-3.31450	1.29138
H	-2.59270	0.60837	0.08438
H	-2.31389	3.07213	0.03223
H	-0.09180	4.10199	-0.12034
H	1.98117	2.68070	-0.12785
H	-0.63882	-1.81401	-0.90233
H	-0.41417	-1.38245	2.06197
H	-0.88603	-3.80715	2.15303
H	-0.70648	-3.82264	0.36251
H	0.72758	-3.48730	1.40915

S_1S_0 CI2

C	0.82234	2.53340	-0.34462
C	0.93172	1.13230	-0.35949
C	-0.19064	0.30051	-0.07069
C	-1.42790	0.92436	0.20043
C	-1.53158	2.30844	0.21810
C	-0.40703	3.10759	-0.04118
O	2.16804	0.64884	-0.61907
C	-0.09493	-1.12536	-0.11302
N	1.10335	-1.75323	-0.32458
C	1.81758	-2.06161	0.86755
H	-2.30863	0.30231	0.39757
H	-2.49307	2.78300	0.42149
H	-0.50964	4.19795	-0.03572
H	1.70907	3.13129	-0.54444
H	-0.99950	-1.72803	0.02928
H	2.09889	-0.23727	-1.07140
H	2.83175	-2.43213	0.61036
H	1.92881	-1.17731	1.52889
H	1.28889	-2.85529	1.43870

Cartesian Coordinates of Ab Initio Structures

The structures have been obtained with the following methods:
Ground-state structures – MP2/cc-pVDZ
Excited-state strucutures – CC2/cc-pVDZ
Conical Intersections – CASSCF(6,6)/cc-pVDZ

α (S_0)

C	0.91552	2.32262	-0.13800
C	0.92106	0.91261	-0.09548
C	-0.32128	0.22361	0.01715
C	-1.52628	0.96089	0.08372
C	-1.51959	2.35799	0.03991
C	-0.28774	3.03476	-0.07186
O	2.10187	0.26871	-0.16295
C	-0.36530	-1.23856	0.06470
N	0.71103	-1.95840	0.00707
C	0.55982	-3.40530	0.06213
H	-2.47273	0.41374	0.17119
H	-2.45788	2.91813	0.09183
H	-0.26564	4.12929	-0.10747
H	1.87774	2.83692	-0.22365
H	-1.36671	-1.70880	0.15269
H	1.87639	-0.70116	-0.11685
H	1.12451	-3.79724	0.92420
H	-0.49872	-3.71871	0.14976
H	0.99392	-3.85109	-0.84809

γ (S_0)

C	0.12302	-0.33440	-3.08994
C	1.33534	-0.47171	-2.45876
C	1.48087	-0.34102	-1.00056
C	0.21040	-0.05260	-0.27789
C	-1.03753	0.08189	-0.98706
C	-1.08796	-0.05369	-2.35448
O	2.57973	-0.46427	-0.43118
C	0.33880	0.06815	1.10151
N	-0.62417	0.32979	1.99907
C	-0.40444	0.39599	3.43264
H	-1.96408	0.29523	-0.43709
H	-2.03746	0.04873	-2.88854
H	0.06739	-0.43993	-4.18007
H	2.25033	-0.68510	-3.02157
H	1.35166	-0.06095	1.50579
H	-0.74886	1.36090	3.84011
H	-0.92979	-0.41947	3.95868
H	0.67373	0.29975	3.62483
H	-1.57698	0.44274	1.66449

δ (S_0)

C	0.81438	0.39455	0.50873
C	-0.54508	0.02270	0.38405
C	-1.47242	0.96946	-0.10142
C	-1.05440	2.24146	-0.51458
C	0.30706	2.58615	-0.41827
C	1.23516	1.67231	0.09859
C	-1.00525	-1.33181	0.80847
N	-0.58098	-2.48541	0.40110
C	0.40853	-2.51913	-0.67628
O	1.76204	-0.44223	1.03154
H	-2.52903	0.68588	-0.17029
H	-1.78132	2.96024	-0.90478
H	0.64780	3.57702	-0.73591
H	2.29345	1.93007	0.20388
H	-1.80698	-1.35766	1.56669
H	1.29335	-1.21168	1.39379
H	0.55632	-1.55442	-1.19513
H	0.07803	-3.27814	-1.40338
H	1.37935	-2.85936	-0.27679

β (S_1)

C	-1.48164	1.08906	0.01390
C	-1.14977	2.46764	-0.07904
C	0.17861	2.85928	-0.11317
C	1.21777	1.86161	-0.04846
C	0.87781	0.53263	0.03107
C	-0.48662	0.08089	0.03872
O	1.90060	-0.45531	0.09415
C	-0.85322	-1.30088	0.11975
N	0.02694	-2.35864	0.19936
C	-0.36072	-3.65188	-0.34933
H	-2.53421	0.78062	0.05574
H	-1.95398	3.21060	-0.11003
H	0.46085	3.91602	-0.17480
H	2.27437	2.15075	-0.05510
H	-1.91668	-1.56987	0.10267
H	0.34144	-4.42314	0.00262
H	-1.36777	-3.90770	0.01895
H	-0.38158	-3.65942	-1.45693
H	1.01281	-2.10058	0.06508

$\gamma\,(S_1)$

C	-1.79892	1.73638	-0.03733
C	-0.80091	2.69374	-0.04453
C	0.58873	2.29821	-0.00059
C	0.89660	0.96252	0.04748
C	-0.10632	-0.05865	0.05969
C	-1.45511	0.35251	0.02047
O	2.25526	0.52349	0.06709
C	0.33597	-1.42113	0.12289
N	-0.52249	-2.48592	0.14056
C	-0.02024	-3.83828	-0.05176
H	-2.25768	-0.39525	0.06759
H	-2.85477	2.02628	-0.06691
H	-1.04290	3.76196	-0.08750
H	1.38581	3.04924	-0.01529
H	1.40024	-1.63850	0.28435
H	-0.78368	-4.56231	0.27181
H	0.25342	-4.05065	-1.10352
H	0.87396	-3.97702	0.57633
H	-1.44734	-2.30370	-0.25083

S_1S_0 CI1

C	0.52710	0.99535	0.09661
C	0.14237	-0.40030	0.22222
C	1.02043	-1.49904	0.17385
C	2.37464	-1.25508	-0.08467
C	2.81073	0.08482	-0.24418
C	1.93790	1.17165	-0.16115
C	-1.28003	-0.41609	0.54108
H	0.65087	-2.52276	0.31688
H	3.08486	-2.08440	-0.15070
H	3.87379	0.27568	-0.43801
H	2.30782	2.19752	-0.27572
O	-0.36202	1.89931	0.21677
N	-2.17515	-0.40951	-0.39885
H	-1.67938	-0.36193	1.56730
H	-1.79151	-0.39889	-1.34896
C	-3.60829	-0.18885	-0.22384
H	-3.85305	0.82320	-0.57902
H	-4.17143	-0.93808	-0.79773
H	-3.84880	-0.27299	0.84414

S_1S_0 CI2

C	0.67186	0.31631	0.31373
C	-0.69860	-0.10463	0.23937
C	-1.66765	0.89095	-0.07465
C	-1.30148	2.19893	-0.36038
C	0.04700	2.56273	-0.31990
C	1.01666	1.60736	0.03414
C	-1.12258	-1.43233	0.47636
H	-2.70952	0.60107	-0.10937
H	-2.05877	2.92859	-0.61258
H	0.34998	3.57668	-0.53966
H	2.06056	1.88017	0.10266
O	1.66026	-0.54568	0.64954
N	-0.30498	-2.50470	0.73769
H	-2.18942	-1.62711	0.54618
H	1.31785	-1.25945	1.17129
C	0.12587	-3.23560	-0.43666
H	0.67166	-2.57921	-1.12079
H	-0.74028	-3.63154	-0.97735
H	0.76757	-4.06205	-0.13644

References

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