Electronic Supporting Information

Demonstration of Baird's Rule Complementarity in the Singlet State with Implications for Photochemical Design.

Bryan J. Lampkin, Yen H. Nguyen, Peter B. Karadakov* and Brett VanVeller*

Department of Chemistry, University of York, Heslington, York, YO10 5DD, United Kingdom
Department of Chemistry, Iowa State University, Ames, Iowa 50011, United States

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Spectroscopic Methods

Absorption and emission spectroscopy: Fluorescence spectra were measured on an Agilent Technologies Cary Eclipse fluorescence spectrophotometer using right-angle detection. Ultraviolet–visible absorption spectra were measured with an Agilent Technologies Cary 8454 UV–vis diode array system and corrected for background signal with a cuvette containing the same solvent used for analysis.

Computational Methods

Computations for Fig. 8 were performed using the Gaussian09 suite.[1] B3LYP and TD-B3LYP were the functional and method of choice.[2, 3] This selection was justified by its use in modeling ESIPT fluorescence[4] as well as by the fact that our own functional screen of HBO absorption showed that B3LYP best matched experiment (Table S1). All optimized geometries were verified to be local minima by the absence of any imaginary frequencies in the vibrational analysis. Ground state and excited state vibrational analyses were done using analytic and numeric methods, respectfully. All geometric and vibrational parameters were determined using the 6-31+G(d) basis set while both ground and excited state electronic energies were determined using a more extended basis set, 6-311+G(d,p).[5] All calculations were obtained using default G09 parameters unless otherwise stated. Excited state geometries were obtained by taking the ground state optimized geometries and subjecting them to TD-DFT geometry optimizations. We restricted these optimizations to the respective first singlet excited states. Absorption values reported were obtained by vertically exciting the ground state optimized geometry from S_0 to S_n while emission values reported were obtained by vertically exciting the relaxed excited state optimized geometry from S_0 to S_n.[6] All reported excited state energies are from the S_1 state. There was no observed switching of orbitals involved in the lowest energy excited states across the ESIPT potential energy surface.

TD-DFT Functional Screen

Table S1. Functional Screen of HBO S_o – S_1 Excitation

	s0-s1 Excitation Energy (eV)	ΔE
experiment	3.721[a]	-
b3lyp	3.8691	0.1481
cam-b3lyp	4.1859	0.3168
LCwPBE	4.3936	0.2077
M062x	4.2393	-0.1543
PBE1PBE	3.969	-0.2703
wB97xD	4.2096	0.2406

Calculated Coordinates

HBO Enol S_0

	X	Y	Z
C	-1.909668	0.646875	-0.000104
C	-1.957643	-0.753872	0.000088
C	-3.133332	-1.487597	0.000189
C	-4.315344	-0.737487	0.000086
C	-4.294835	0.670603	-0.000108
C	-3.095541	1.386595	-0.000206
C	0.113406	-0.081713	-0.00003
H	-3.136517	-2.572725	0.000338
H	-5.270141	-1.255644	0.000157
H	-5.237001	1.211691	-0.000181
H	-3.07823	2.472101	-0.000353
C	1.555516	-0.209335	-0.000032
C	2.179314	-1.474059	-0.000146
C	2.359699	0.962314	0.000085
C	3.56248	-1.586384	-0.000152
H	1.556226	-2.363017	-0.000232
C	3.757189	0.835161	0.000076
C	4.348668	-0.422605	-0.000041
H	4.030002	-2.566462	-0.000239
H	4.353003	1.742789	0.000169
H	5.432894	-0.501303	-0.000045
N	-0.571673	1.035072	-0.00015
O	-0.659946	-1.216608	0.000148
O	1.844458	2.209059	0.000221
H	0.855921	2.156492	0.000261

Energy -706.045492636 ht

HBO Keto S_0

	X	Y	Z
C	-1.951393	-0.762345	0.000084
C	-1.897317	0.636008	0.000006
C	-3.06524	1.394402	-0.000068
C	-4.274662	0.688658	-0.000041
C	-4.31158	-0.714885	0.000032
C	-3.134416	-1.47748	0.000103
C	0.175363	-0.184072	-0.000006

H	-3.038673	2.479275	-0.000088
H	-5.208229	1.243692	-0.000061
H	-5.270768	-1.22388	0.000043
H	-3.146714	-2.562243	0.000136
C	1.574482	-0.252043	-0.000077
C	2.292978	1.025381	-0.000029
C	2.270688	-1.495673	-0.000131
C	3.730913	0.924903	0.00006
C	3.643422	-1.522135	-0.000037
H	1.698734	-2.420018	-0.000136
C	4.366619	-0.293115	0.000096
H	4.287739	1.85747	0.00008
H	4.177475	-2.467538	-0.000001
H	5.454502	-0.324831	0.000159
N	-0.544262	0.952867	0.000111
O	-0.656044	-1.259518	0.000031
O	1.693513	2.148909	-0.000159
H	0.036875	1.827253	0.000157

Energy -706.026821884 ht

HBO Enol S_1

	X	Y	Z
C	-1.893169	0.644606	0.000097
C	-1.97314	-0.772939	-0.0001
C	-3.160564	-1.478466	-0.00014
C	-4.339585	-0.704888	0.000023
C	-4.290526	0.702631	0.000221
C	-3.082863	1.403363	0.000264
C	0.121567	-0.149653	-0.000122
H	-3.182586	-2.56345	-0.000287
H	-5.302905	-1.206635	-0.000001
H	-5.224045	1.259586	0.000344
H	-3.05108	2.488363	0.000415
C	1.537353	-0.26669	-0.000112
C	2.235327	-1.481692	-0.000006
C	2.343523	0.953639	-0.000083
C	3.653682	-1.510932	0.000179
H	1.677923	-2.412313	-0.00002
C	3.752054	0.902067	0.000125

C	4.416211	-0.333887	0.000264
H	4.152474	-2.476231	0.000277
H	4.290903	1.844393	0.000141
H	5.500242	-0.375785	0.000412
N	-0.576484	1.004623	0.000074
O	-0.691934	-1.275143	-0.000214
O	1.756691	2.143847	-0.000356
H	0.737182	2.017117	-0.000889

Energy -705.90895572 ht

HBO Keto S_1

	X	Y	Z
C	-1.970353	-0.754419	0.000015
C	-1.941314	0.649241	-0.000108
C	-3.132536	1.394356	-0.00011
C	-4.325172	0.652606	0.000033
C	-4.337698	-0.74742	0.000157
C	-3.136586	-1.497079	0.000145
C	0.152225	-0.134059	-0.000155
H	-3.130677	2.478873	-0.000218
H	-5.271185	1.187412	0.000036
H	-5.287355	-1.273798	0.000257
H	-3.127469	-2.581247	0.000242
C	1.596921	-0.225383	-0.000079
C	2.364158	1.015397	-0.000028
C	2.247964	-1.442227	-0.000119
C	3.785077	0.891452	0.000114
C	3.685234	-1.527249	-0.00006
H	1.668994	-2.362192	-0.000239
C	4.434393	-0.368064	0.000066
H	4.357579	1.814348	0.000306
H	4.156298	-2.505081	-0.00009
H	5.520078	-0.412576	0.000168
N	-0.602317	0.982958	-0.000266
O	-0.663577	-1.222354	-0.000027
O	1.775697	2.153422	0.000346
H	-0.10087	1.88209	-0.000371

Energy -705.919838633 ht

NAP Enol S_0

	X	Y	Z
C	2.758526	0.553797	-0.000014
C	2.454815	-0.812189	0.000044
C	3.407447	-1.818653	0.000105
C	4.740185	-1.390223	0.000088
C	5.073236	-0.021714	0.000023
C	4.092561	0.972658	-0.000023
C	0.603793	0.355956	-0.000213
H	3.137984	-2.86985	0.000149
H	5.534186	-2.131498	0.000126
H	6.121038	0.265615	0.000022
H	4.349006	2.027573	-0.00005
C	-0.820426	0.640956	-0.00011
C	-1.867548	-0.367661	-0.000066
C	-1.187739	2.007545	-0.000029
C	-1.636649	-1.772181	-0.000128
C	-3.237716	0.061339	0.000047
C	-2.553353	2.396052	0.000082
C	-2.682882	-2.677779	-0.000082
H	-0.626952	-2.152743	-0.000212
C	-4.287573	-0.891993	0.000091
C	-3.541731	1.45291	0.000118
H	-2.769982	3.4595	0.000139
C	-4.02463	-2.245429	0.000028
H	-2.459307	-3.741822	-0.000133
H	-5.313088	-0.528743	0.000177
H	-4.585743	1.757948	0.000208
H	-4.836169	-2.967914	0.000063
O	1.083016	-0.933102	0.00002
N	1.562599	1.259426	0.000001
O	-0.313865	3.026006	-0.000042
H	0.615738	2.662373	-0.000091

Energy -859.688097079

NAP Keto S_0

	X	Y	Z
C	2.774045	0.547133	0.000032
C	2.458106	-0.813875	-0.000142

C	3.408793	-1.817305	-0.000127
C	4.746452	-1.394566	0.000078
C	5.081394	-0.031209	0.000252
C	4.101578	0.969385	0.000229
C	0.546226	0.307955	-0.000094
H	3.133353	-2.866665	-0.000267
H	5.536585	-2.139374	0.000093
H	6.128477	0.257528	0.0004
H	4.363813	2.022484	0.000353
C	-0.820597	0.62022	0
C	-1.894232	-0.371747	0.000017
C	-1.124037	2.054085	0.00009
C	-1.694433	-1.774473	-0.000024
C	-3.245971	0.092116	0.000091
C	-2.524451	2.433781	0.000025
C	-2.765477	-2.660011	0.000014
H	-0.692599	-2.179159	-0.000078
C	-4.315878	-0.827559	0.00012
C	-3.514655	1.506257	0.000085
H	-2.731728	3.499582	-0.000064
C	-4.089698	-2.194505	0.000087
H	-2.566804	-3.729107	-0.000014
H	-5.33256	-0.439675	0.000163
H	-4.556254	1.823489	0.000092
H	-4.921803	-2.893203	0.000111
O	1.07846	-0.948897	-0.000321
N	1.556042	1.209513	-0.000078
O	-0.236974	2.960789	-0.000255
H	1.252358	2.208289	-0.000031

Energy -859.677383604 ht

NAP Enol S_1

	X	Y	Z
C	2.746414	0.558244	0.000045
C	2.448373	-0.824969	-0.000043
C	3.404388	-1.822081	-0.000061
C	4.742144	-1.387482	0.000015
C	5.070463	-0.015147	0.000104
C	4.092034	0.977574	0.000121

C	0.582911	0.339203	-0.000053
H	3.140306	-2.874685	-0.000126
H	5.538564	-2.126059	0.000005
H	6.118345	0.272894	0.000159
H	4.346074	2.03289	0.000187
C	-0.805054	0.622292	-0.000053
C	-1.872377	-0.370671	-0.000026
C	-1.198158	2.045999	-0.000034
C	-1.645426	-1.76861	-0.000049
C	-3.244045	0.080067	0.000042
C	-2.5373	2.426679	0.000035
C	-2.69719	-2.702925	-0.000014
H	-0.632837	-2.143447	-0.000097
C	-4.278505	-0.880836	0.000078
C	-3.549639	1.466479	0.000075
H	-2.759195	3.488772	0.000047
C	-4.016841	-2.258472	0.00005
H	-2.46739	-3.764335	-0.000035
H	-5.308137	-0.530108	0.00013
H	-4.591444	1.775138	0.000127
H	-4.842198	-2.965362	0.000079
O	1.082496	-0.959649	-0.000092
N	1.574466	1.253903	0.00003
O	-0.289176	3.02445	-0.000131
H	0.636928	2.626496	-0.000307

Energy -859.566916014 ht

NAP Keto S_1

	X	Y	Z
C	2.778927	0.562854	0.000024
C	2.470188	-0.806861	-0.00001
C	3.425511	-1.806698	-0.000036
C	4.766682	-1.370947	-0.000026
C	5.092736	-0.005745	0.000011
C	4.113046	0.996139	0.000038
C	0.549378	0.309794	0.00001
H	3.156762	-2.857466	-0.000062
H	5.562184	-2.110053	-0.000045
H	6.139547	0.285532	0.00002

H	4.37056	2.04999	0.000068
C	-0.84355	0.61429	0.00002
C	-1.891711	-0.35993	0.000012
C	-1.190794	2.067684	0.000028
C	-1.664131	-1.775749	0.000001
C	-3.279454	0.096197	0.000014
C	-2.571092	2.432391	-0.000009
C	-2.705178	-2.687103	-0.000003
H	-0.650125	-2.148295	-0.000005
C	-4.307261	-0.863521	0.00001
C	-3.578967	1.487695	-0.000001
H	-2.785452	3.496529	-0.00004
C	-4.040563	-2.230687	0.000004
H	-2.490734	-3.751818	-0.000012
H	-5.337923	-0.515946	0.000009
H	-4.621953	1.794078	-0.000017
H	-4.861821	-2.942483	0
O	1.095506	-0.948394	-0.000013
N	1.56721	1.210255	0.000042
O	-0.278919	2.956038	-0.000089
H	1.27319	2.208174	0.000078

Energy -859.563201528 ht

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